

TO: Commissioner of Patents and Trademarks Washington, D.C. 20231	REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT
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In compliance with the Act of July 19, 1952 (66 Stat. 814; 35 U.S.C. 290) you are hereby advised that a court action has been filed on the following patent(s) in the U.S. District Court:

DOCKET NO. 3:91cv1480-6	DATE FILED 5-24-96	U.S. DISTRICT COURT Northern District of TX - Dallas Division
PLAINTIFF Advanced Display Systems Inc		DEFENDANT Kent State University Kent Research Corporation Kent Display Systems
PATENT NO.	DATE OF PATENT	PATENTEE
1 5,453,863	9/26/95	ADS
2		
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SOLICITOR
OCT 14 1997

U.S. PATENT & TRADEMARK OFFICE

In the above-entitled case, the following patent(s) have been included:

DATE INCLUDED 10/8/97	INCLUDED BY <input checked="" type="checkbox"/> Amendment <input type="checkbox"/> Answer <input type="checkbox"/> Cross Bill <input checked="" type="checkbox"/> Other Pleading		
PATENT NO.	DATE OF PATENT	PATENTEE	
1	<div style="border: 1px solid black; border-radius: 50%; padding: 10px; display: inline-block;"> See attached form 26 pat Nos </div>		
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In the above-entitled case, the following decision has been rendered or judgment issued:

DECISION/JUDGMENT

CLERK NANCY DOHERTY	(BY) DEPUTY CLERK 	DATE OCT - 9 1997
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NORTH HAVEN DISTRICT COURT
T COURT
OF TEXAS
OCT - 8 1997
NANCY DOHERTY, CLERK
By Deputy

ADVANCED DISPLAY SYSTEMS, INC.

Plaintiff,

v.

**KENT STATE UNIVERSITY,
KENT RESEARCH CORPORATION, and
KENT DISPLAY SYSTEMS**

Defendants/Third Party Plaintiffs

V.

Bao-Gang Wu

Third Party Defendant

**CIVIL ACTION NO.
3-96-CV-1480-BD (G)**

(consolidated with
CIVIL ACTION NO.
3-96-CV-1608-BD)

35 U.S.C. §282 NOTICE

Pursuant to the provisions of 35 U.S.C. §282, Plaintiff Advanced Display Systems, Inc. (“ADS”) and Third Party Defendant Bao-Gang Wu (“Wu”) hereby give notice to Defendants/Third Party Plaintiffs of the following patents (including their prosecution histories), and publications they will rely upon as anticipations of the patents in suit or as showing the state of the art:

PATENTS

<u>Country</u>	<u>Number</u>	<u>Date</u>	<u>Patentee</u>
U.S.	4,097,127	06/27/78	Haas, et al.

together with the following U.S. Patents specifically incorporated by reference:

(i) U.S. Patent No. 3,704,056, November 28, 1972, Wysocki, et al.;

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(ii) U.S. Patent No. 3,652,148, March 28, 1972, Wysocki, et al.; and

(iii) U.S. Patent No. 3,909,114, September 30, 1975, Haas, et al.

U.S.	3,821,720	06/28/74	Greubel, et al.
U.S.	3,680,950	08/01/72	Haas, et al.
U.S.	3,642,348	02/15/72	Wysocki, et al.
U.S.	3,703,331	11/21/72	Goldmacher, et al.
U.S.	3,806,230	04/23/74	Haas
U.S.	3,707,322	12/26/72	Wysocki, et al.
U.S.	3,711,713	01/16/73	Wysocki, et al.
U.S.	3,718,382	02/27/73	Wysocki, et al.
U.S.	3,718,380	02/27/73	Wysocki, et al.
U.S.	5,625,477	04/29/97	Wu, et al.
U.S.	5,661,533	08/26/97	Wu, et al.
U.S.	5,437,811	08/01/95	Doane, et al.
U.S.	5,384,067	01/24/95	Doane, et al.
U.S.	4,671,618	06/09/87	Wu, et al.
U.S.	4,673,255	06/16/87	West, et al.
U.S.	4,685,771	08/11/87	West, et al.
U.S.	4,688,900	08/25/87	Doane, et al.
U.S.	4,890,902	01/02/90	Doane, et al.
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U.S.	5,240,636	08/31/93	Doane, et al.
U.S.	5,251,048	10/05/93	Doane, et al.
PCT	PCT/US85/00397	08/03/95	Doane, Joseph W.
PCT	PCT/US93/09999	10/19/93	Doane, Joseph W. et al.

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1. G.A. Dir et al., "Cholesteric Liquid Crystal Texture Change Displays," 1971 SID Digest of Technical Papers, pp. 132-133.
2. Frederic J. Kahn, "Electric-Field-Induced Color Changes and Pitch Dilation in Cholesteric Liquid Crystals", Physical Review Letters, Vol.24(5), February 2, 1970, pp. 209-212.
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ADS and Wu further give notice that Mr. Werner E. Haas may be relied upon as the prior inventor or as having prior knowledge of or as having previously used and offered for sale the invention of the patent in suit, U.S. Patent No. 5,453,863. Mr. Werner E. Haas resides at 768 Hightower Way, Webster, New York 14580.

Respectfully submitted,

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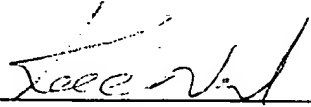
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CERTIFICATE OF SERVICE

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Cholesteric reflective display: Drive scheme and contrast

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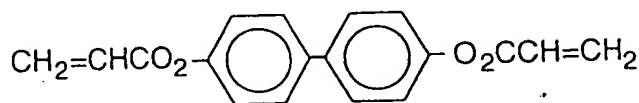
(Received 27 October 1993; accepted for publication 24 January 1994)

We studied the electro-optical response of a bistable cholesteric texture (BCT) display to ac voltage pulses. The material can be driven into states where planar and focal conic textures coexist at zero field and gray scale memory is achieved. According to the properties of the BCT display we designed two drive schemes; one for binary operation and the other for gray scale operation. We made a 320×320 pixel reflective display with a resolution of 80 lines/in. on a passive matrix. Measurement in an integration chamber showed that the display has higher contrast and better viewing angle than a reflective super twisted nematic display.

P. 1905 - 1907

The bistable cholesteric texture (BCT) display has two stable optical contrasting states at zero field;¹⁻⁴ one state reflects colored light and the other state is weakly scattering. The reflecting and scattering states correspond to the planar and focal conic textures, respectively. In the planar texture the liquid crystal is a periodic helical structure with the helix axes perpendicular to the surface of the cell and reflects light of wavelength $\lambda = nP$, where n is the average refractive index and P is the pitch length.⁵ In the focal texture the liquid crystal is in a poly-domain structure with the helix axes oriented randomly throughout the cell and scatters light weakly. A BCT display cell typically has a cell gap of a few μm and the back plate of the cell is painted black. In the planar texture the cell reflects colored light while in the focal conic texture the cell is almost transparent and appears black because of the painted black background. The transformation between the reflecting and black states of a cell can be achieved by application of an ac voltage pulse whereby the reflecting state is obtained after the application of a high voltage pulse and the black state is obtained after the application of a low voltage pulse. The cholesteric material can be used to make high definition flat panel displays on a passive matrix because of its bistability.⁶ The display does not need polarizers and can be operated in front-lit conditions. The reflected light is brilliant under room light conditions.

The liquid crystal used in our experiment is a mixture of E48, CB15, ZLI4572, and CE1. E48 is a nematic liquid crystal and CB15, ZLI4572, and CE1 are chiral agents. The mixture reflects green light and the color shift in the temperature region of 0–80 °C is less than 30 nm. The display cell consists of two indium tin oxide (ITO) glass plates and the cell gap is controlled by 5- μm glass fiber spacers. The ITO glass plates are coated with polyimide and buffed for the homogeneous alignment of the liquid crystal. Small amounts of a biacrylate monomer and photoinitiator are added to the mixture. The monomer has the structure shown below:



The monomer is polymerized under ultraviolet (UV) irradiation to form a cross-linked network. The function of the polymer is to stabilize the focal conic texture, reported as polymer-stabilized cholesteric textures (PSCT) display,³ and to improve the optical contrast of the display.⁴

We studied the response of the PSCT display cell to pulses of various voltages to examine the gray scale using the following procedure: First, we drove the cell into the reflecting state or the scattering state; then we applied a pulse of certain voltage to the cell. Finally, we measured the reflection of the cell 2 s after the application of the pulse in order to obtain a stable value. In the experiment the incident unpolarized light was monochromatic (tuned to the reflection peak) and collimated. The incident angle was 22.5° and the reflected light was detected with a collection cone of 70° centered at the reflection angle of 22.5°. The intensity of the reflected light was normalized to that of the incident light. The width of the applied pulse was 20 ms. The result is shown in Fig. 1 where curve a is the response of the cell in the reflecting state prior to the pulse. For voltage below 20 V, the reflection is not affected by the pulse. When the voltage of the pulse is between 20 and 34 V, the reflection decreases approximately linearly with the increasing voltage. Stable gray scale is obtained in this region. The reflection of the cell reaches its original value when the voltage is above 46 V. Curve b is the response of the cell in the scattering state prior to the pulse. In this case the reflection of the cell is unchanged by the pulse of voltage below 44 V. The cell is switched into the reflecting state by a pulse of voltage above 50 V.

We measured the iso-contrast of PSCT displays in an integration chamber where the incident light was isotropic and unpolarized. The result is shown in Fig. 2. The PSCT

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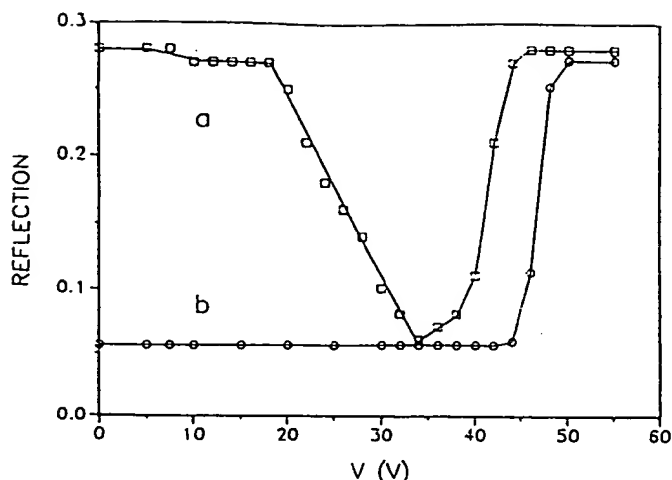


FIG. 1. Reflection of the PSCT cell vs the voltage of applied pulse. The reflection was measured 2 s after the application of the pulse. (a) The cell is in the planar texture prior to the pulse; (b) the cell is in the focal conic texture prior to the pulse.

display has no polarizers and therefore the contrast is symmetric about the azimuthal angle. In Fig. 3 the contrast of the PSCT display is plotted versus the polar angle. The contrast of a reflective STN (super twisted nematic) is also shown for the purpose of comparison. The PSCT display has a higher contrast and better viewing angle than the STN.

We designed two drive schemes for the PSCT display: one for binary displays and the other for gray scale displays. For the binary display, let us consider an example of a 3×3 pixel display shown in Fig. 4 to illustrate the drive scheme. The voltages given here are for the display whose electro-optical property is shown in Fig. 1. The row voltage is either 35 V for the selected row or 0 V for the nonselected row. The column voltage is $V_R = 15$ V for obtaining the reflecting state and 0 V for obtaining the scattering state. The row and column voltages are ac square pulse and have opposite phases. Hence, for the pixels in the selected row the voltage across the pixel is either 50 V to obtain the reflecting state or 35 V

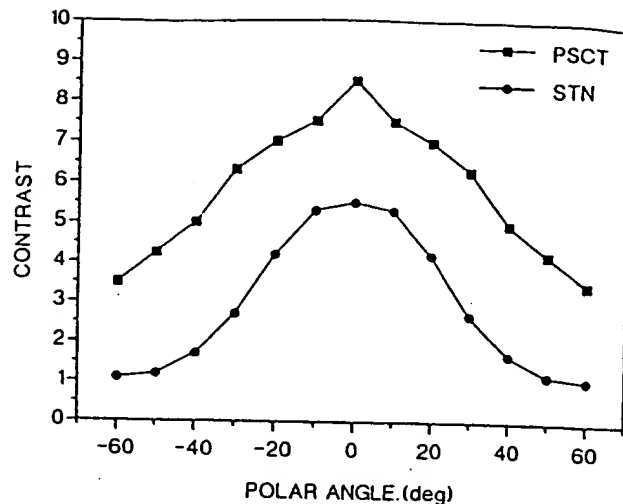


FIG. 3. Contrast of the PSCT cell and reflective STN cell vs the polar angle where the incident light is isotropic and unpolarized.

to obtain the scattering state. For the pixels in the nonselected row the voltage across the pixel is either 0 or 15 V under which the states of the pixels are unchanged. Therefore once a pixel of a multiplexed display is addressed into the reflecting or scattering state, it will remain in that state. The contrast ratio of the image is independent of the number of rows. We made a 320×320 pixel display with a resolution of 80 lines/in. A picture of Escher's Water Fall on the PSCT display is shown in Fig. 5. In this drive scheme there is, however, a problem that the frame time is long and not fast enough for video rate operation.

For the gray scale display, first the display has to be refreshed, that is, a high voltage pulse applied to all the pixels to drive them into the reflecting state. The row voltage is 20 V for the selected row and 0 V for the nonselected row. The column voltage is between 0 and 15 V, depending on the gray scale. The row and column voltages are ac square pulses and have opposite phases. The voltage across the pixel

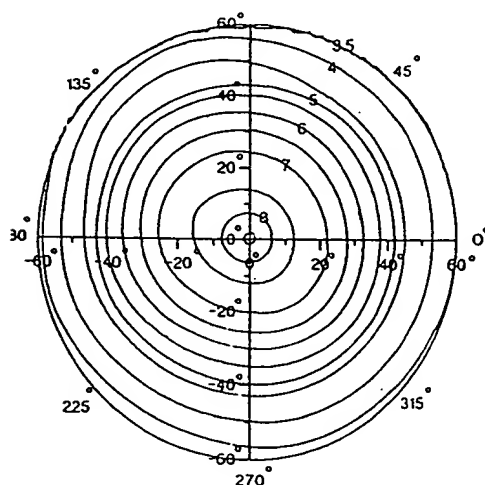


FIG. 2. Iso-contrast of the PSCT cell where the incident is isotropic and unpolarized.

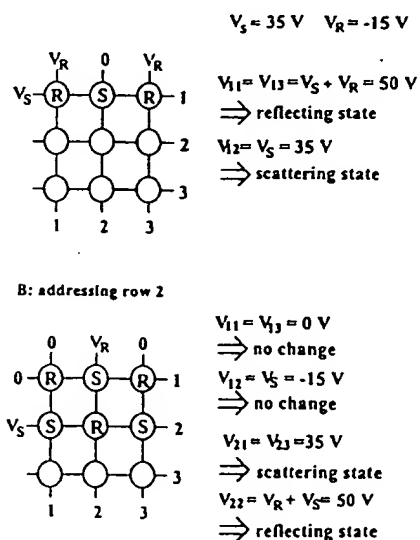


FIG. 4. Drive scheme for binary PSCT displays.

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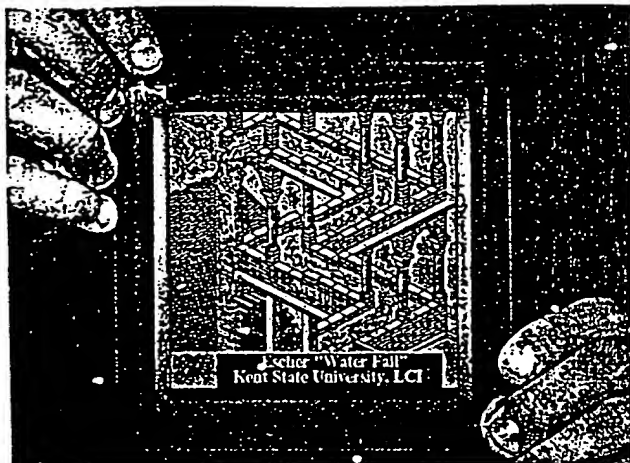


FIG. 5. Photograph of Escher Water Fall on the 320×320 pixel PSCT display.

els on the selected row is between 20 and 35 V, where the gray scale is obtained. The voltage across the pixels on the nonselected row is between 0 and 15 V and therefore the states of the pixels are unchanged.

We have demonstrated that BCT material has gray scale

memory and can be used to make high definition displays on passive matrices. There is no cross-talking effect and the contrast ratio is independent of the number of rows. The BCT display does not need polarizers and can be operated in front-lit condition. The display looks brilliant under room light conditions. BCT has a higher contrast and wider viewing angle than the reflective STN. The thickness tolerance for the binary display is small and the manufacturing cost is low. The dynamic response time of the BCT material is, however, fast enough for video rate operation with the passive drive scheme. Research is under way to improve the response time and design new drive scheme.

This research was supported in part by the NSF Science and Technology Center ALCOM under Grant No. DMR89-20147.

¹D.-K. Yang, L.-C. Chien, and J. W. Doane, Conf. Res. IDRC. SID, San Diego, CA, 1991, p. 49.

²D.-K. Yang and J. W. Doane, SID Dig. Tech. Papers, 759 (1992).

³J. W. Doane, D.-K. Yang, and Z. Yaniv, in Proceedings of the 12th International Display Research Conference, Hiroshima, Japan, 1992, p. 73.

⁴D.-K. Yang, J. West, L.-C. Chien, and J. W. Doane (unpublished).

⁵See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, London, 1974).

⁶E. Kaneko, *Liquid Crystal TV Displays: Principles and Applications of Liquid Crystal Displays* (KTK Scientific, Tokyo, 1986), pp. 77–90.

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Cholesteric reflective display: Drive scheme and contrast

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(Received 27 October 1993; accepted for publication 24 January 1994)

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The liquid crystal used in our experiment is a mixture of E48, CB15, ZLI4572, and CE1. E48 is a nematic liquid crystal and CB15, ZLI4572, and CE1 are chiral agents. The mixture reflects green light and the color shift in the temperature region of 0–80 °C is less than 30 nm. The display cell consists of two indium tin oxide (ITO) glass plates and the cell gap is controlled by 5- μm glass fiber spacers. The ITO glass plates are coated with polyimide and buffed for the homogeneous alignment of the liquid crystal. Small amounts of a biacrylate monomer and photoinitiator are added to the mixture. The monomer has the structure shown below:



The monomer is polymerized under ultraviolet (UV) irradiation to form a cross-linked network. The function of the polymer is to stabilize the focal conic texture, reported as polymer-stabilized cholesteric textures (PSCT) display,³ and to improve the optical contrast of the display.⁴

We studied the response of the PSCT display cell to pulses of various voltages to examine the gray scale using the following procedure: First, we drove the cell into the reflecting state or the scattering state; then we applied a pulse of certain voltage to the cell. Finally, we measured the reflection of the cell 2 s after the application of the pulse in order to obtain a stable value. In the experiment the incident unpolarized light was monochromatic (tuned to the reflection peak) and collimated. The incident angle was 22.5° and the reflected light was detected with a collection cone of 70° centered at the reflection angle of 22.5°. The intensity of the reflected light was normalized to that of the incident light. The width of the applied pulse was 20 ms. The result is shown in Fig. 1 where curve a is the response of the cell in the reflecting state prior to the pulse. For voltage below 20 V, the reflection is not affected by the pulse. When the voltage of the pulse is between 20 and 34 V, the reflection decreases approximately linearly with the increasing voltage. Stable gray scale is obtained in this region. The reflection of the cell reaches its original value when the voltage is above 46 V. Curve b is the response of the cell in the scattering state prior to the pulse. In this case the reflection of the cell is unchanged by the pulse of voltage below 44 V. The cell is switched into the reflecting state by a pulse of voltage above 50 V.

We measured the iso-contrast of PSCT displays in an integration chamber where the incident light was isotropic and unpolarized. The result is shown in Fig. 2. The PSCT

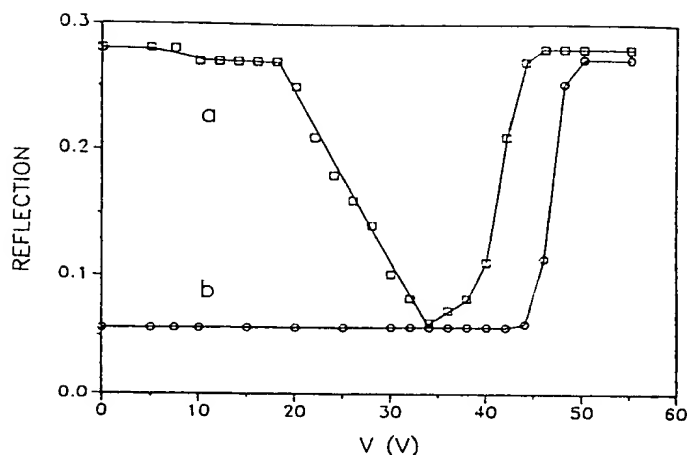


FIG. 1. Reflection of the PSCT cell vs the voltage of applied pulse. The reflection was measured 2 s after the application of the pulse. (a) The cell is in the planar texture prior to the pulse; (b) the cell is in the focal conic texture prior to the pulse.

display has no polarizers and therefore the contrast is symmetric about the azimuthal angle. In Fig. 3 the contrast of the PSCT display is plotted versus the polar angle. The contrast of a reflective STN (super twisted nematic) is also shown for the purpose of comparison. The PSCT display has a higher contrast and better viewing angle than the STN.

We designed two drive schemes for the PSCT display: one for binary displays and the other for gray scale displays. For the binary display, let us consider an example of a 3×3 pixel display shown in Fig. 4 to illustrate the drive scheme. The voltages given here are for the display whose electro-optical property is shown in Fig. 1. The row voltage is either 35 V for the selected row or 0 V for the nonselected row. The column voltage is $V_R = 15$ V for obtaining the reflecting state and 0 V for obtaining the scattering state. The row and column voltages are ac square pulse and have opposite phases. Hence, for the pixels in the selected row the voltage across the pixel is either 50 V to obtain the reflecting state or 35 V

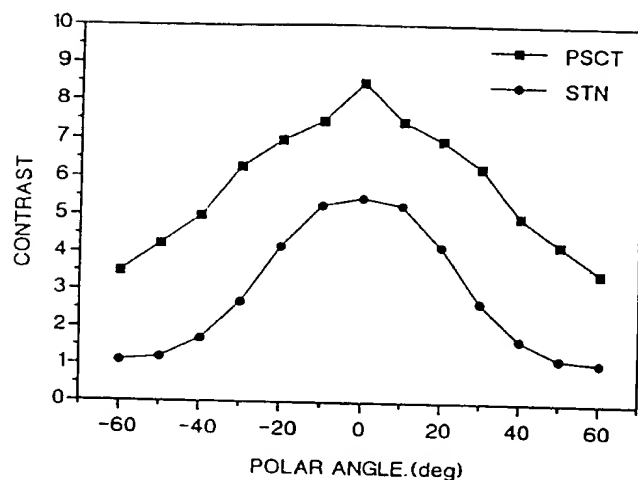


FIG. 3. Contrast of the PSCT cell and reflective STN cell vs the polar angle, where the incident light is isotropic and unpolarized.

to obtain the scattering state. For the pixels in the nonselected row the voltage across the pixel is either 0 or 15 V under which the states of the pixels are unchanged. Therefore once a pixel of a multiplexed display is addressed into the reflecting or scattering state, it will remain in that state. The contrast ratio of the image is independent of the number of rows. We made a 320×320 pixel display with a resolution of 80 lines/in. A picture of Escher's Water Fall on the PSCT display is shown in Fig. 5. In this drive scheme there is, however, a problem that the frame time is long and not fast enough for video rate operation.

For the gray scale display, first the display has to be freshened, that is, a high voltage pulse applied to all the pixels to drive them into the reflecting state. The row voltage is 20 V for the selected row and 0 V for the nonselected row. The column voltage is between 0 and 15 V, depending on the gray scale. The row and column voltages are ac square pulses and have opposite phases. The voltage across the pix-

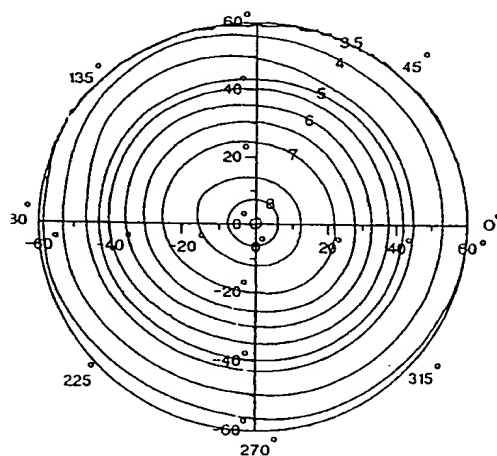


FIG. 2. Iso-contrast of the PSCT cell where the incident is isotropic and unpolarized.

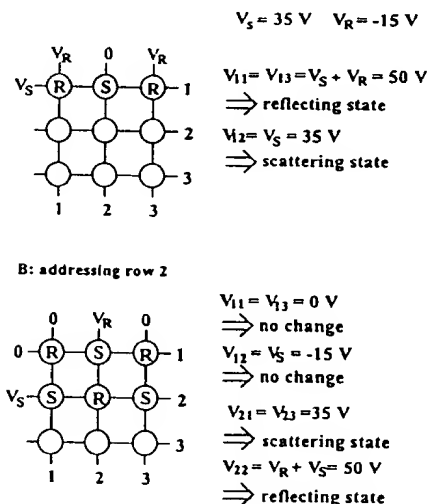


FIG. 4. Drive scheme for binary PSCT displays.

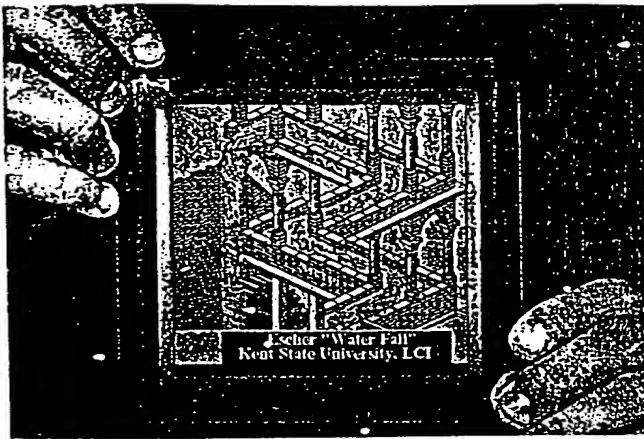


FIG. 5. Photograph of Escher Water Fall on the 320×320 pixel PSCT display.

els on the selected row is between 20 and 35 V, where the gray scale is obtained. The voltage across the pixels on the nonselected row is between 0 and 15 V and therefore the states of the pixels are unchanged.

We have demonstrated that BCT material has gray scale

memory and can be used to make high definition displays on passive matrices. There is no cross-talking effect and the contrast ratio is independent of the number of rows. The BCT display does not need polarizers and can be operated in front-lit condition. The display looks brilliant under room light conditions. BCT has a higher contrast and wider viewing angle than the reflective STN. The thickness tolerance for the binary display is small and the manufacturing cost is low. The dynamic response time of the BCT material is, however, fast enough for video rate operation with the passive drive scheme. Research is under way to improve the response time and design new drive scheme.

This research was supported in part by the NSF Science and Technology Center ALCOM under Grant No. DMR89-20147.

¹D.-K. Yang, L.-C. Chien, and J. W. Doane, Conf. Res. IDRC. SID, San Diego, CA, 1991, p. 49.

²D.-K. Yang and J. W. Doane, SID Dig. Tech. Papers, 759 (1992).

³J. W. Doane, D.-K. Yang, and Z. Yaniv, in Proceedings of the 12th International Display Research Conference, Hiroshima, Japan, 1992, p. 73.

⁴D.-K. Yang, J. West, L.-C. Chien, and J. W. Doane (unpublished).

⁵See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, London, 1974).

⁶E. Kaneko, *Liquid Crystal TV Displays: Principles and Applications of Liquid Crystal Displays* (KTK Scientific, Tokyo, 1986), pp. 77–90.

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Patent Abstracts of Japan

PUBLICATION NUMBER : JP52113386
PUBLICATION DATE : 22-09-77
APPLICATION NUMBER : JP760030475
APPLICATION DATE : 19-03-76

VOL: 2 NO: 15 (C - 002)
AB. DATE : 31-01-1978 PAT: A 52113386
PATENTEE : DAINIPPON PRINTING CO LTD;
others: 01
PATENT DATE: 22-09-1977

INVENTOR : IZAWA AKIRA; others: 01

INT.CL. : C09K3/34
G02F1/13; G09F9/00; G09F9/30

TITLE : STABILIZED LIQUID CRYSTAL
COMPOSITION

ABSTRACT : PURPOSE: To produce a mixed liquid crystal composition for memory type liquid crystal display by adding limited amounts of alkyl halides and/or F-contg. surfactants to a mixed liquid crystal comprising specific amounts of nematic and cholesteric liquid crystals.

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日本国特許庁
公開特許公報

特許出願公開
昭52-113386

50Int. Cl.² 識別記号 52日本分類 庁内整理番号 特許公開 昭和52年(1977)9月22日
C 09 K 3/34 # 1 0 2 13(9) C 0 7229-4A
G 02 F 1/13 101 E 5 7013-54 発明の数 1
G 09 F 9/00 101 E 9 7129-54 審査請求 未請求
G 09 F 9/30 104 G 0 7348-23

(全 8 頁)

安定化液晶組成物

特 願 昭51-30475

出 願 昭51(1976)3月19日

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明 細 書

発明の名称

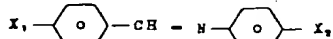
安定化液晶組成物

特許請求の範囲

1.(a) ネマチック液晶70~95重量%とコレステリック液晶5~30重量%とからなる混合液晶、および

(b) 該混合液晶基準で0.01~10重量%のアルキルハライドおよび/または電解系界面活性剤を含むことを特徴とする、安定化されたメモリー型液晶組成物。

2. 前記ネマチック液晶が、一般式

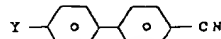


(X₁, X₂はそれぞれ、炭素数1~12のアルキル基、炭素数1~9のアルコキシ基、シアノ基から選ばれ、)のシッフ液晶化合物の少くとも1種を含む特許請求の範囲第1項記載の組成物。

3. 前記ネマチック液晶が、前記混合液晶基準で、40~60重量%のp-メトキシベンジリデン-p-

ブチルアニリン、20~40重量%のp-エトキシベンジリデン-p-ブチルアニリン、および7~20重量%のp-ヘキシルオキシベンジリデン-p-シアノアニリンまたはp-ブトキシベンジリデン-p-シアノアニリン、からなる特許請求の範囲第2項に記載の組成物。

4. 前記ネマチック液晶が一般式



(Yは炭素数4~13のアルキルもしくはアルコキシ基、または炭素数5~30のフェニル基もしくはアルコキシフェニル基)で表わされるビフェニル液晶化合物の少くとも一種を含む、特許請求の範囲第1項記載の組成物。

5. 前記ネマチック液晶が一般式



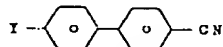
(Z₁, Z₂はそれぞれシアノ基、炭素数3~8のフェニル基、炭素数4~8のアルコキシ基から選ばれ、ともてアルキル基であり得るが、ともてシアノ基あるいはアルコキシ基ではあり得ない)であるフェニルベンゾエート液晶化合物の少くとも一

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値を含む、特許請求の範囲第1項記載の組成物。

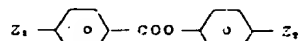
6. 前記ネマチック液晶が、前記混合液晶基中で、

(i) 一般式



(I:炭素数4~15のアルキルもしくはアルコキシ基、または炭素数5~30のアルキルフェニル基もしくはアルコキシフェニル基)で表わされるとフェニル液晶化合物の少くとも一種/〜30重量%;および

(ii) 一般式



(Z₁, Z₂は、それぞれシアノ基、炭素数3~5のアルキル基、炭素数4~8のアルコキシ基から選ばれ;ともにアルキル基であり得るが、ともにシアノ基あるいはアルコキシ基ではあり得ない)であるフェニルベンゾエート系液晶化合物の少くとも一種50~94重量%;とからなる、特許請求の範囲第1項記載の組成物。

発明の詳細な説明

本発明はメモリー型液晶表示一すなわち境界線

に電流の流れる必要がないので寿命も長いという特徴を有する。しかしながら偏光板の使用が必要であるため表示は暗く、さらに表示に方向性があり、いわゆる視角が狭い、という欠点がある。

これらの表示方法に対し、メモリー型液晶表示として、ネマチック液晶にコレステリック液晶を含む組成物に十〜数十Vの直流または交流電圧を加えると白濁を生じ動的散乱による表示と同様の表示状態が得られ、この白濁は印加電圧を除いた後も維持され、メモリー効果を示すこと;またこのメモリー状態の液晶に数MHzの低周波電圧を印加するか、セルに機械的圧力を加えて液晶相に流れを生ずるか、あるいは表示メモリー化電圧の約2〜5倍程度の電圧を印加した交流電圧を急激に0にする方法により、上記白濁が除かれること、すなわちメモリーの消去が行われること;が知られている。上記白濁は境界効果によるものであり、本質的に電流が流れる必要はない。その上メモリー効果と考えると、このメモリー型液晶表示に要する単位時間当りの消費電力は極めて小さくなる

印加時には透明であるが、境界印加により白濁し、この状態を印加電圧を取り除いた後も維持し得る液晶の性質を利用した表示に用いる新規なネマチック-コレステリック混合液晶組成物に関する。

従来、ネマチック液晶を用いた表示装置としては、自の誘電異方性を有するロッドネマチック液晶を用いた動的散乱効果による表示と;正の誘電異方性を有するプレートネマチック液晶と偏光板を用いた境界効果による表示;の2つのタイプがあった。

動的散乱効果による表示は、液晶層に電流を流した時に生ずる液晶分子の回転、運動等に基づく光の散乱効果を表示に用いたものであり;境界効果による表示に比べ表示が明るいという特徴があるが、表示に10〜数十V、数十μA/cm²と比較的に大電圧、大電流を要し、消費電力が境界効果型に比べるかに大きくなる難点を有する。また、本質的に電流が必要である為、反電圧を生じやすく、寿命が短くなりやすいという欠点がある。

一方境界効果による表示は駆動電圧が1〜数Vと低く、電流も約1μA/cm²と小さい。また本質的

ことが期待できる。また表示は偏光板が不要であり、表示が明るく視角が広いという特徴がある。

しかしながらこのネマチック-コレステリック混合液晶には、ネマチック液晶成分とコレステリック液晶成分の間に分子構造上の非互に大きな差違があり、安定な混合液晶の維持という点で問題がある。すなわち表示と消去の繰り返しにより、しだいに各液晶成分に相分離するなどの劣化を生じ混合初期に比べて、表示電圧、消去電圧および応答速度の変化ならびにメモリー特性の劣化などの劣化変化が認められ、さらには表示が認められなくなるような割合さえある。さらに、この混合液晶を用いるメモリー型液晶表示には、前記した動的散乱効果による表示あるいは境界効果による表示に比べて、表示あるいは消去の応答性が悪いという欠点がある。

本発明者らは、上記したような従来のネマチック-コレステリック混合液晶の欠点を解決することを目的として研究を進めた結果、特定の有機ハロゲン化合物を添加することにより上記欠点が著し

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く改められることを見出し本願発明に到達したものである。

すなわち、本発明のメモリー型液晶組成物は、

(a) ネマチック液晶70〜95重量%とコレステリック液晶5〜30重量%とからなる混合液晶、および

(b) 該混合液晶系中で0.01〜10重量%のアルキルハライドおよび/または高沸点有機溶剤を含むことを特徴とするものである。

このようにして、上記した特定の有機ハロゲン化合物を添加して得られた本発明の液晶組成物をメモリー型液晶表示素子として用いる場合には、次のような効果が得られるものである。

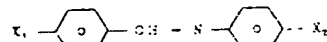
- (1) 表示電圧、消去電圧、応答速度、メモリー特性などの長期安定化が図れる。
- (2) 上記特性の安定化に加えて、表示電圧および消去電圧の低下、ならびに応答速度の高速化が得られる。
- (3) 作動温度範囲、特に低温度域、が上げられる。
- (4) また、表示のときのスレシホールド電圧の

安定性が著しく改善される。

以下、本発明のメモリー型液晶組成物を更に詳細に説明する。

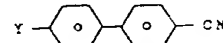
本発明の液晶組成物中のネマチック液晶成分としては、従来ネマチック液晶特性を示すものとして知られている任意の化合物を単独で、あるいは二つ以上併用して用いることができる。既知の液晶特性を有するものの特徴的性質を有するものとを混ざない。このようなネマチック液晶化合物の例として、たとえば以下のものがあげられる。

一般式



(ここで、 X_1, X_2 はそれぞれ炭素数1〜8のアルキル基もしくはアルコキシ基、またはシアノ基)で表わされるシラフイ結化合物、たとえばp-ブチルベンジリデン-p'-シアノアニソール、p-ブチルベンジリデン-p'-エトキシアニソールなど；

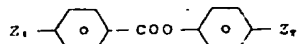
一般式



(Y：炭素数4〜15のアルキルもしくはアルコキシ基)

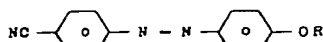
シ基、または炭素数8〜30のアルキルフェニル基もしくはアルコキシフェニル基)、また、ビフェニル液晶化合物、たとえばp-ベンチル-p'-シアノビフェニル、p-ヘキシルオキシ-p'-シアノビフェニル、p-ブチル-p'-p'-シアノフェニル)ビフェニルなど；

一般式



(Z_1, Z_2 は、それぞれ炭素数1〜8のアルキル基；炭素数4〜8のアルコキシ基、シアノ基から選ばれ；ともにアルキル基であり得るが、ともにシアノ基、アルコキシ基でないことが好ましい)で表わされるフェニルベンゾエート液晶化合物、たとえばp'-シアノフェニル-p'-シアノベンゾエート、p-ベンチルオキシ-p'-ヘキシルベンゾエートなど；

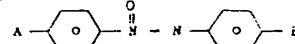
一般式



(Rは炭素数4〜8のアルキル基)で表わされるアゾ系液晶化合物、たとえばp'-シアノ-p'-ヘ

キシルオキシアゾベンゼン；

一般式



(A, B：それぞれ炭素数4〜8のアルキル基またはアルコキシ基、シアノ基)で表わされるアゾ系液晶化合物、たとえばp-ブチル-p'-ブチルアゾキシベンゼン、p-ヘキシルオキシ-p'-シアノアゾキシベンゼンなど。

上記ネマチック液晶化合物中の溶媒系としてのアルキル基およびアルコキシ基は前記であることが好ましい。

以上のネマチック液晶化合物のうち、ビフェニル液晶化合物もしくはフェニルベンゾエート液晶化合物の少くとも1種をネマチック液晶成分として用いると、表示(特にメモリー化のための駆込み)電圧、消去電圧を著しく低下することが可能であり、また液晶の化学的安定性にもすぐれるので好ましい。また、このビフェニル液晶化合物とフェニルベンゾエート液晶化合物を、混合液晶(コレステリック液晶も含む)系中で、それぞれ

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1~30重量部および50~95重量部の割合で混合すれば、得られる表示素子の作動温度範囲を広げる効果ならびに応答速度の迅速化の向上が得られる。

また、混合原料中のコレステリック液体として、コレステロールの誘導体：たとえばコレステリルホルメイト、コレステリルアセテート、コレステリルプロピオネート、コレステリルブチレート、コレステリルバレレート、コレステリルヘキサノエート、コレステリルヘプタノエート、コレステリルオクタノエート、コレステリルノナノエート、コレステリルデカノエート、コレステリルウンデシレート、コレステリルドデシレート、コレステリルミリスチレート、コレステリルパルミチレート、コレステリルマルガレート、コレステリルスチアレート、コレステリルエルケート、コレステリルオレエート、コレステリルリノレート、コレステリルリノリネート、コレステリルクロトネート、ジコレステリルセバケート、ジコレステリルアジベート等の脂肪カルボン酸エステル；コレステリルベンゾエート、コレステリル-p-ニトロ

ベンゾエート、コレステリルジニトロベンゾエート、コレステリルシンナメート、コレステリルアニソエート、ジコレステリルフタレート等の芳香族カルボン酸エステル；コレステリルシクロヘキサノカルボキシレート、コレステリル-2-フロエート等の脂肪族カルボン酸エステル；コレステリルメチルカーボネート、コレステリルエチルカーボネート、コレステリルメトキシエチルカーボネート、コレステリル-2,2,2-トリフロエチルカーボネート、コレステリルジデシルカーボネート、コレステリル-2-(2-メトキシエトキシ)エチルカーボネート、コレステリル(2-エトキシエトキシ)エチルカーボネート、コレステリル-2-(2-ブトキシエトキシ)エチルカーボネート、コレステリルデカニルカーボネート、コレステリルシンナミルカーボネート、コレステリルアリルカーボネート、コレステリルノタリルカーボネート、コレステリルクロチルカーボネート、コレステリルオレイルカーボネート、コレステリルノリルカーボネート、コレステリル

-2-プロピル-1-イルカーボネート、コレステリル-2-メチル-2-プロペン-1-イルカーボネート、等の炭酸エステル；さらにはコレステリルクロライド、コレステリルブロマイド、コレステリルニトレート等の他の無機物のエステルがあげられる。

上記コレステリック液体は少なくとも一種が用いられる。

本発明のメタリ-誘導体組成物に用いる混合原料は、上記エマチック液体とコレステリック液体をそれぞれ70~95重量部対5~30重量部に配合することにより得られる。エマチック液体が混合原料中の、70重量部では応答性が悪くなり、場合によっては表示が生じず、また原料が相分離し易くなる。また95重量部を超えるとメモリー性を失い、場合によっては表示も生じないことがある。

本発明では上記した混合原料に添加剤としてその0.01~10重量部のアルキルハライドおよび/または非水系界面活性剤を加える。

アルキルハライドとしては、室温で液体のフッ

化アルキル、塩化アルキル、臭化アルキル、ヨウ化アルキルが用いられる。炭素数8以上の塩化アルキル、炭素数3以上の臭化アルキル、炭素数1以上のヨウ化アルキル等が挙げておける作用性、溶解性との相性がよく、加えるの安定性が良いので好ましい。アルキル基は直鎖でつと、分岐のものでもよいことをいわず、また炭素数の上ではアルキルハライドを炭素数何個で構成するかにて定められ、好ましくは10以下である。このような、アルキルハライドとしては、たとえば、ヨウ化エチル、ヨウ化丁ミル、ヨウ化ヘキシル、臭化ブチル、臭化ヘプチル、臭化アミル、塩化ヘプチル、塩化デシルなどがあげられる。

また非水系界面活性剤としては非水系液体に可溶性であり、表面活性を示すものであれば、ノニオン系、アニオン系、カチオン系又は両性のいずれの非水系界面活性剤をも用いることができ、たとえばフルオロアルコキシポリフルオロアルキル炭酸エステル、フルオロカーボンスルホン酸塩、フルオロカーボンカルボン酸塩などのアニオン系界

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面活性剤、たとえばN-フルオロアルキルスルホンアミドアルキルアミン*級アンモニウム塩、N-フルオロアルキルスルホンアミドアルキルアミン塩、N-フルオロアルキルアミドアルキルアミン*級アンモニウム塩、N-フルオロアルキルアミドアルキルアミン塩、N-フルオロアルキルスルホンアミドアルキルハロメチルエーテル*級アンモニウム塩などのカチオン系界面活性剤、たとえばフルオロカーボンスルホンアミド、フルオロカーボンアミノスルホンアミド、フルオロカーボンカルボキシスルホンアミド、フルオロカーボンヒドロキシスルホンアミド、フルオロカーボンスルホンアミドエチレンオキサイド付加物、フルオロカーボンヒドロキシスルホンアミド酸塩エステル、フルオロカーボンアミノ酸アミド、フルオロカーボン酸アミド、フルオロカーボンヒドロキシ酸アミド、フルオロカーボン酸アミドのエチレンオキサイド付加物塩、フルオロカーボンヒドロキシ酸アミド酸塩エステル、フルオロカーボンヒドロキシ酸アミド酸塩エステル、フルオロカーボ

ンスルホン酸、フルオロハイドロカーボンカルボン酸、フルオロハイドロカーボンアルキルエステル、フルオロハイドロカーボンカルボキシアルキルエステル、フルオロカーボンヒドロキシアミド、フルオロハイドロカーボンアルキルエステル酸塩、フルオロアルキルジアミンなどのアニオン系界面活性剤、たとえばベタイン系フルオロカーボンスルホンアミド結合を有するアルキルアミン、ベタイン系フルオロカーボン酸アミド結合を有するアルキルアミンなどの両性界面活性剤があげられる。

本発明の界面活性剤の例としては、メソジナ・マニ・フアクチュアリング・アンド・マイニング・カンパニー（以下メソジナと略称する）から、PC[®]系別として販売されているPC75（パーフルオロオクタスルホン酸カリウム塩）、あるいはPC125（フルオロカーボンカルボキシスルホンアミドカリウム塩）、PC170（ポリオキシエチレンフルオロカーボンスルホンアミド）、PC431（ポリオキシエチレンフルオロカーボンアミド）など

が挙げられる。

上記アルキルハライドおよび/または界面活性剤を活性剤は、それぞれ二種以上あるいはそれぞれ二種以上を選んでそれらの混合物として用いることもでき、その混合物として前記配合液系液で0.01~10重量部添加される。添加量が0.01重量部未満では本発明の効果が得られず、10重量部を超えると液相を破壊する危険性があるので好ましくない。さらに詳しくいえば、アルキルハライドのみを用いるときは0.5~10重量部、界面活性剤のみを用いるときは0.01~5重量部の範囲で用いることが好ましい。

本発明の最終組成物には、上記の加剤とともに、アルキルスルホニウム塩、ハイドロキノンエステル塩、アルキルアンモニウム塩などの有機塩類、さらにはその他の公知の添加剤を加えることができる。この場合にも、添加剤の量や、本発明の添加剤も含めて前記配合液の10重量部を超えないことが好ましくない。

本発明の組成物は、上記した各成分を必要

に比例して、液状を保持しつつ貯留することにより得られる。加剤する場合に不溶性成分は、液状の状態で貯留することが好ましい。

このようにして得られた本発明の組成物は、表示が良好な、電子時計、クロックなどの電子時計、あるいは電子式車上計具などの計測器表示素子として用いた場合に好ましい。

以下、実施例、比較例を挙げて本発明をさらに具体的に示す。例中では重量部を示し、液体成分のアルキル系、アルコキシ系は同様のものとする。

比較例1

重量のp-メトキシベンジリデン-β-ブチルアニリン45~55部、p-エトキシベンジリデン-β-ブチルアニリン25~35部、p-ヘキシルオキシベンジリデン-β-シアノアニリン10~15部、およびコレステリルノナノエート5~15部よりなる配合液(A)を真空中で、110℃以上に加圧で重合し、一對のネサガラス電極間に厚さ10~20ミクロンのマイラー・フィルムをスペーサーとして両

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み込み；さらに該一對のネオガラスをエポキシ樹脂で接着固定して表示セルを構成した。こうして得られたセルの一對の電極間に32Hzの矩形波電圧を印加したところ10~15V（表示電圧）で白濁状態となった。特に15~20Vの印加電圧（メモリー化電圧）では電圧除去後も白濁が残り、いわゆるメモリー状態が得られた。一万40V以上の電圧を印加すると白濁は得られなかった。

また上記したようにメモリー状態にあるセルに付して40V以上の電圧（消去電圧）を印加すると白濁状態は直ちに消滅状態となり、この状態で印加電圧を急激に0Vすると透明状態が保たれた。

しかしながら、上記セルに20秒間1秒の割合で20Vと45Vの32Hzの矩形波電圧を交互に繰り返し印加して、表示・消去の繰り返しによる寿命試験を行ったところ、3~10日で表示状態にむらが生じ、更に寿命試験を続けると表示の認められなくなる部分が現われた。この表示が認められなくなった部分を顕微鏡で観察したところ液晶相に分離が認められた。

ト2番、p-シアノフェニル-p-ブチルベンゾエート15番、p-シアノフェニル-p'-ペンチルベンゾエート3番、p-シアノフェニル-p-ヘキシルベンゾエート20番、p-シアノフェニル-p'-ヘプチルベンゾエート20番、p-シアノフェニル-p-オクタチルベンゾエート20番およびp-ヘキシルオキシ-p'-ブチルベンゾエート20番からなるフェニルベンゾエート系メタチック液晶93番と、コレステリルクロライド7番とを、真空中でN15以上に加減圧を混合して、液晶相液晶を得た。

得られた液晶相液晶を適量の溶剤で作られた表示セル中に注入し、表示電圧および対向電極間、真流または交流電圧を印加したところ、3~13Vで白濁状態となり、特に7~12Vの電圧ではメモリー化が得られた。このメモリー状態は13V以上の交流電圧の印加により消去され透明状態にもどった。

しかし、50Hzのサイン波による交流電圧10Vおよび20Vを交互に30秒に2秒の割合で印加した

実験例-1

比較例-1で用いた液晶相(A)に、その0.5重量部のヨウ化エチルを添加して液晶相液晶を得た。この液晶相液晶を用いて比較例-1と同様にセルを組み立てた。

得られたセルを用いて、比較例-1と同様に表示・消去試験をしたところ、メモリー化電圧7~20V、消去電圧35V以上の結果が得られた。またこのセルを用いて比較例-1と同様に寿命試験をしたところ、90日間の試験によっても表示からそのほの電圧は同様に認められなかった。

このヨウ化エチルの添加量を0.05量としても同様の効果は認められ、また10量まで添加しても同様の効果は認められ、寿命は改善された。

さらにヨウ化エチルの代わりに重量部3~10の直鎖または分岐のヨウ化アルキル、臭化アルキル、あるいは重量部3~10のヨウ化アルキルを用いても同様の効果が認められた。

比較例-2

p-シアノフェニル-p'-プロピルベンゾエー

とところ1カ月で表示状態にむらを生じ、おぼろげによる液晶相に分離が認められた。

実験例-2

上記液晶相液晶(B)にその0.1量の3M社製フッ素系界面活性剤PC-170（ポリオキシエチレンフルオロカーボンスルホアミド）を添加し、比較例-2と同様にセルを組み立てた。得られたセルを用いて比較例-2と同様に試験したところ、同様の表示および消去電圧が得られ、寿命試験テストにおいても3カ月たっても表示から液晶相の分離は全く認められなかった。

またPC-170の添加量を3量まで添加したところ、液晶相での液晶相増加が抑制され、使用可能寿命が伸びた。

さらにPC-170の代わりに、同じ3M社製のPC-95、-98、-126、-128、-134、-176、-430、-431を用いてテストしてみても同様の結果が得られた。

比較例-3

p-ペンチル-p'-シアノビフェニル80番、p

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ヘキシル- β -シアノビフェニル/6多および
ヘキシルオキシ- β -シアノビフェニル/6多からなるビフェニル系ホモナフタレン系47番と、コレステリルクロレート/3多を加え真空中で加熱昇華重合して重合膜を得た。

この重合膜を用いて比較例-1と同様にセルを形成し、32Hzの正弦波電圧を加え、30V以下での割合で10Vでメモリー化、20Vで消去を交互に行う運転試験を行ったところ約2週間表示を維持した。

実施例-3

上記重合膜10枚、その0.5量のPC-431(ポリオキシエチレンフルオロカーボンアミド)を添加して重合膜を得た。重合膜10枚のみでは約10V以下で結露の色上昇と、さらには発熱現象が生じたが、この重合膜では発熱現象となる発熱が抑制された。この低電圧での結露上昇の抑制効果は、PC-431の添加量の増加に従って増大した。

この組成物を用いて比較例-3と同様にセルを形成し、書き込み電圧10V、消去電圧20Vで運転試験

を行ったところ、3カ月経過後も表示むらや発熱現象の分離は認められなかった。

PC-431の代わりに、PC-95、-98、-126、-128、-134、-170、-176、-430を加えた場合も同様の効果が認められた。

比較例-4

β -シアノフェニル- β -ブチルベンゾエート47番、 β -シアノ- β -ヘプタールビフェニル21番および β -シアノフェニル- β -ヘキシルベンゾエート32番からなるホモナフタレン系(ビフェニル)重合体とフェニルベンゾエート重合体との混合物)の90番とコレステリルノナノエート10番とからなる重合膜を得た。比較例-1と同様にセルを形成し、比較例-1と同様に表示むら及び発熱試験を行ったところ、表示電圧3~10V、メモリー化電圧3~7V、消去電圧10V以上の結果が得られた。表示、消去に要する電圧値はそれぞれ1~2Vおよび0.5V程度であった。またメモリー化電圧および消去電圧をそれぞれ6Vおよび12Vとした以外は比較例-1と同様にして運転試験を行った。

たところ、3カ月で表示むらが発生した。

実施例-4

重合膜10枚、その0.5量の塩化アミンを添加し、得られた重合膜を用いて、比較例-4と同様にセルを形成し、表示試験を行ったところ、表示電圧値が2Vまで下がり、発熱現象の安定化が見られた。

また上記組成物にPC-95(パーフルオロオクタスルホンカルリウム塩)を0.2多添加して同様にセルを形成し、表示試験を行ったところ、表示および消去に要する電圧値はともに比較例-4の場合の $1/2 \sim 1/3$ に低減された。さらに、このセルを用いて比較例-4と同様に運転試験を行ったところ、3カ月経過後も表示むらや発熱現象の分離は認められなかった。

実施例-5

比較例-2で用いた重合膜10枚にその1量の臭化ブチルおよび1量のヨウ化ヘキシルを加えて組成物を付した。

この組成物を用いて、比較例-2と同様にセル

を形成し、表示試験を行ったところ、表示電圧3~12V、メモリー化電圧7~12V、消去電圧15V以上の結果が得られた。

また、このセルを用いて比較例-2と同様に運転試験を行ったところ、3カ月経過後も表示むらの発生、発熱現象の分離は認められなかった。

実施例-6

比較例-3で用いた重合膜10枚、その0.5量のPC-128(フルオロカーボンカルボキシスルホンカルリウム塩)および0.5量のヘプタールクロライドを添加して組成物を付した。

この組成物を用いて、比較例-3と同様にセルを形成した。得られたセルで、32Hzの正弦波電圧を加えて表示、消去試験を行ったところ、同一条件下で比較例-3のセルを用いたときと比べて表示電圧3~12V、メモリー化電圧、消去電圧15V以上であったのに対し、表示電圧2~12V、メモリー化電圧3~7V、消去電圧13~15Vの結果が得られた。

また、このセルを用いて、比較例-3と同様に運転試験を行ったところ、3カ月経過後も表示

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示むらや電基相の分離は認められなかった。

また、この組成物には低濃度での粘着増加の抑制効果も認められた。

実施例-7

p-ペンチル-p'-シアノビフェニル79.8g、
p-アミロキシ-p'-シアノビフェニル2.0g、
p-ヘキシル-p'-シアノビフェニル15.3g、p-
ヘブチルオキシ-p'-シアノビフェニル1.4g、
p-オクタノキシ-p'-シアノビフェニル1.3
g、p-ブチル-p'-(p'-シアノビフェニル)ビ
フェニル0.2gからなる混合液を、0.05gの
PC-78および0.1gのPC-128を添加して溶液を
得た。

この溶液を用いて、比較例-3と同様にセル
を作した。得られたセルに3250電圧を印
加して表示、消去試験を行ったところ、同一条件
で比較例-3のセルを用いたときは表示電圧3
~12V、メモリー化電圧、消去電圧15V以上であ
ったのに対し、表示電圧3~12V、メモリー化電
圧3~7V、消去電圧13~15Vの結果が得られた。

また、このセルを用いて、比較例-3と同様に
連続駆動試験を行ったところ、3カ月経過後も表
示むらや電基相の分離は認められなかった。

また、この組成物には低濃度での粘着増加の
抑制効果も認められた。

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Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Veröffentlichungsnummer:

0 123 981**A2**

(12)

EUROPÄISCHE PATENTANMELDUNG

(21) Anmeldenummer: 84104098.3

(51) Int. Cl.³: **G 02 F 1/137**

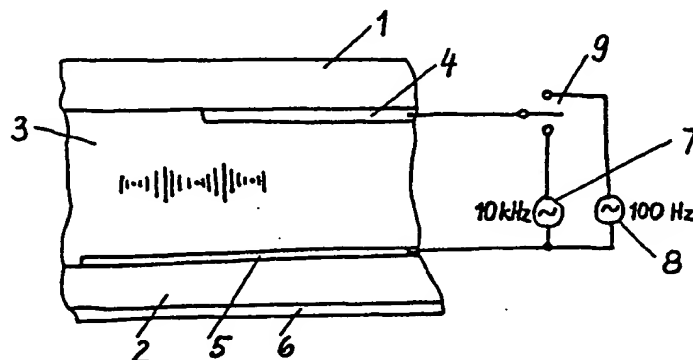
(22) Anmeldetag: 12.04.84

(30) Priorität: 29.04.83 CH 2319/83

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W. Meizer Steinsdorfstrasse 10, D-8000 München 22 (DE)(54) **Flüssigkristallzelle.**

(57) Zwischen zwei Trägerplatten mit Ansteuerelektrode ist ein cholesterischer Flüssigkristall angeordnet, der in zwei optisch verschiedenen, stabilen Texturen existiert und eine dielektrische Anisotropie besitzt, die bei niedrigen Frequenzen positiv, bei höheren Frequenzen negativ ist, wodurch der Flüssigkristall durch Anlegen einer niederfrequenten Spannung

eine der beiden stabilen Texturen und durch Anlegen einer höherfrequenten Spannung die andere stabile Textur annimmt. Die beiden optisch verschiedenen Texturen sind ohne anliegende Spannung langzeitstabil. Dadurch sind energiesparende Anzeigen möglich.



ACTORUM AG

EP 0 123 981 A2

RAN 4701/116

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Flüssigkristallzelle

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Die Erfindung betrifft eine Flüssigkristallzelle zur optischen Darstellung elektrischer Signale mit einem cholesterischen Flüssigkristall zwischen zwei mit Ansteuer-
elektroden versehenen Trägerplatten.

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Flüssigkristallzellen mit cholesterischen Flüssigkristallen sind bekannt. Bei diesen Zellen wird der Umstand benutzt, dass cholesterische Flüssigkristalle in mehreren, d.h. in der Regel in zwei optisch unterschiedlichen Zustandsformen existieren, zwischen denen sie durch Anlegen
25 geeigneter Spannungen hin- und hergeschaltet werden können.

30

In einer Zelle, ohne anliegende elektrische Spannung ist im allgemeinen eine Zustandsform stabil, bei welcher die Moleküle im wesentlichen parallel zu den Trägerplatten liegen, und somit die cholesterische Helixachse im wesentlichen normal auf der Substratebene steht. Zustandsformen, die eine derartige Molekülanordnung aufweisen, werden in der Literatur meistens als Grandjean- oder planare Texturen bezeichnet. Da diese Begriffe aber einerseits für eine theore-
35 tische Idealform der entsprechenden Textur stehen, andererseits aber in der Praxis häufig auch noch zur Bezeichnung mehr oder weniger deformierter Texturen herangezogen werden

und damit zu Missverständnissen Anlass geben können, werden sie für den Zweck der vorliegenden Beschreibung vermieden. Statt dessen wird jeweils die Richtung der Helixachse für die Beschreibung einer Textur benutzt.

5 Bei der zweiten hier interessierenden Struktur liegt die Helixachse im wesentlichen parallel zu den Trägerplatten. Diese Textur liegt wegen der ungünstigen Anpassungsverhältnisse in den Randzonen energetisch höher als diejenige mit platten-
10 normaler Helixachse. Deshalb bildet sich bei kleinem Verhältnis von Zellendicke d zu cholesterischer Schraubungshöhe P dieser Zustand ohne angelegtes Feld allmählich wieder in die stabilere Textur mit plattennormaler Helixachse zurück. Bei grossen Werten von $\frac{d}{P}$ (typisch grösser als zehn) ist der Einfluss der Randzone jedoch so gering, dass sich die
15 Textur mit plattenparalleler Helixachse auch über Tage hinweg nicht zurückbildet. In diesen Fällen scheint sogar die Frage nach der grösseren Stabilität einer der beiden Texturen noch offen zu sein.

Die optischen Eigenschaften der beiden Zustände sind
20 sehr unterschiedlich. Die Textur mit plattennormaler Helixachse reflektiert entweder links- oder rechtsdrehendes zirkular polarisiertes Licht der Wellenlängen λ um den Wert $\bar{n} \cdot P$, wobei \bar{n} mittlere Brechungsindex ist. Für einen höheren Reflexionskoeffizienten muss dabei gelten, dass $d \cdot \Delta n$ grösser
25 als die Wellenlänge ist, wobei Δn die Anisotropie des Brechungsindex ist. Die zweite, nicht reflektierte zirkular polarisierte Komponente des einfallenden Lichts durchquert die Textur im wesentlichen ungestört. Vor absorbierendem Hintergrund erscheinen für $\bar{n} \cdot P$ im sichtbaren Wellenlängenbereich
30 die typischen cholesterischen Reflexionsfarben.

Der Flüssigkristall im Zustand mit plattenparalleler Helixachse dagegen lässt Licht unreflektiert passieren, wobei jedoch eine Vorwärtsstreuung in einem engen Winkelbereich eintritt. Vor absorbierendem Hintergrund erscheint
35 die Flüssigkristallschicht in diesem Zustand deshalb dunkel.

Diese beiden Zustände zeigen vor gut absorbierendem Hintergrund und bei gut entspiegelten Oberflächen einen eindrucklichen Kontrast. Auch in Transmission lässt sich ein guter Kontrast erreichen, wenn wenig dispergierendes Licht so durch Blenden geführt wird, dass das im Zustand mit plattenparalleler Helixachse gestreute Licht die Blenden nicht mehr passieren kann. In dieser Betriebsweise wird die Reflexionseigenschaft des Zustandes mit plattennormaler Helixachse nicht benötigt.

- 10 Die beiden vorstehend definierten Texturen und ihre optischen Eigenschaften wurden schon anfangs unseres Jahrhunderts beschrieben. Einer Verwendung der durch sie bestimmten optischen Unterschiede stand jedoch der Nachteil entgegen, dass es nicht gelang, die beiden Zustände
15 auf einfache Weise in beiden Richtungen ineinander überzuführen, etwa durch elektrische Felder.

- Aus der US-Patentschrift Nr. 3,642,348 ist es bekannt, dass ein cholesterischer Flüssigkristall, der sich im Ruhestand in der Grandjean-Textur befindet, durch Anlegen
20 eines Gleichspannungs- oder eines niederfrequenten Wechselspannungsfeldes in die fokalkonische Textur umgewandelt werden kann. Nach Reduzierung oder Abschalten des Feldes relaxiert der Kristall wieder in seinen Ruhestand, die Grandjean-Textur. Diese Rückbildung kann innerhalb von
25 Sekundenbruchteilen erfolgen, kann sich aber auch über Stunden erstrecken. Sie kann durch mechanische Massnahmen oder durch Erhitzen beschleunigt werden.

- Aus der deutschen Offenlegungsschrift 25 38 212 ist bekannt, dass die Texturumwandlung vom Grandjean- in den fokalkonischen Zustand unter Mitwirkung eines elektrohydrodynamischen Effekts erfolgt, der sich in dielektrisch negativem nematischem Material bei genügend niedrigen Frequenzen einstellt.

- Aus der US-Patentschrift Nr. 3,680,950 ist es bekannt, einen
35 Flüssigkristall mit negativer Dielektrizitäts-Anisotropie durch den orientierenden Effekt eines höherfrequenten elektrischen

Wechselfeldes aus dem fokalkonischen in den Grandjean-Zustand umzuschalten.

5 Damit weisen alle diese Effekte, wenn man sie zu einer in beiden Richtungen schaltbaren Anzeigezelle kombiniert, einen erheblichen Nachteil auf: Infolge des Stromflusses, der die elektrohydrodynamischen Turbulenzen hervorruft, wird der Flüssigkristall langsam, aber kontinuierlich zersetzt. Seine Lebensdauer ist gering.

10 Es ist zu beachten, dass es sich bei dem hier interessierenden Effekt und den vorstehend erwähnten bekannten Effekten um den Texturwechsel innerhalb der cholesterischen Phase und nicht um davon grundsätzlich verschiedene Phasenwechseleffekte handelt.

15 Bei Phasenwechseleffekten weist der Flüssigkristall nur in einem der beiden Schaltzustände eine cholesterische Struktur auf, während er bei angelegtem Haltefeld homöotrop-nematisch ist.

20 In der Deutschen Auslegeschrift Nr. 25,42,189 ist beispielsweise eine solche Zelle beschrieben, die ein cholesterisches Flüssigkristallgemisch enthält, das eine energetisch stabile fokalkonische Struktur aufweist, wenn kein elektrisches Feld anliegt, und aus diesem Zustand in eine homöotrop-nematische Struktur umgeschaltet werden kann, in der es bei Anlegen eines geeigneten Haltefeldes bleibt. Nach Abschalten
25 des Haltefeldes geht der Flüssigkristall wieder in den stabilen fokalkonischen Zustand über.

30 Abgesehen davon, dass dieser Phasenwechseleffekt vom hier betrachteten Texturwechsel grundsätzlich verschieden ist, weist auch der Phasenwechsel so erhebliche Nachteile auf, dass er bisher keine technische Anwendung gefunden hat, obwohl er seit langem bekannt ist. Ausserdem sind für den Phasenwechsel eine sehr hohe Ansteuerspannung und für die Aufrechterhaltung des nicht-stabilen Zustands eine hohe Haltespannung erforderlich.

Der Erfindung liegt die Aufgabe zugrunde, eine Flüssigkristallzelle bereitzustellen, die durch die orientierende Wirkung elektrischer Felder zwischen zwei stabilen, optisch verschiedenen Zuständen geschaltet werden kann und bei der
5 kein Ionenstrom im Flüssigkristall fließen muss, so dass gut isolierende Flüssigkristall-Materialien gebraucht werden können, um Degradationserscheinungen zu vermeiden.

Erfindungsgemäss wird dies dadurch erreicht, dass bei
10 einer Zelle der eingangs genannten Art der Flüssigkristall in zwei optisch verschiedenen stabilen Texturen existiert und eine dielektrische Anisotropie besitzt, die bei Frequenzen unterhalb eines Schwellwerts positiv ist, wodurch der Flüssigkristall durch Anlegen einer Wechselspannung mit
15 einer solchen niedrigen Frequenz eine der beiden stabilen Texturen annimmt, bei Frequenzen oberhalb des Schwellwerts negativ ist, wodurch der Flüssigkristall durch Anlegen einer Wechselspannung mit einer solchen höheren Frequenz in den anderen stabilen Zustand übergeht.

20 . Der cholesterische Flüssigkristall ist vorzugsweise ein Gemisch aus nematischen Flüssigkristallen mit cholesterischen Zusätzen.

Die beiden stabilen Zustandformen, in denen sich der Flüssigkristall befindet, sind die Textur mit plattenparalleler Helixachse, die der Flüssigkristall beim Anlegen einer
25 Niederfrequenzspannung annimmt, und die Textur mit platten-senkrechter Helixachse, in die der Flüssigkristall bei Anlegen einer höherfrequenten Spannung übergeht.

Die dem Flüssigkristall zugewandte Oberfläche der
30 oberen Platte, d.h. der Platte, durch die der Lichteinfall erfolgt, weist vorzugsweise eine homogene Wandorientierung auf. Die gewünschten elektro-optischen Effekte treten jedoch auch in Zellen ein die keine, bzw. homöotrope oder auch hydride Wandorientierungen aufweisen.

Nachfolgend werden anhand der beiliegenden Zeichnungen Ausführungsformen der Erfindung beschrieben. Es zeigen

- Fig. 1 eine schematische Darstellung einer Zelle mit einem cholesterischen Flüssigkristall mit plattenparalleler Helixachse
- 5 Fig. 2 eine schematische Darstellung einer Zelle mit einem Flüssigkristall mit plattennormaler Helixachse
- Fig. 3 eine schematische Kurve des Verlaufs der dielektrischen Anisotropie in Abhängigkeit von der Frequenz eines am Flüssigkristall anliegenden elektrischen Feldes.
- 10 Fig. 4 eine schematische Darstellung einer mit dem neuen Effekt zu verwirklichenden Matrixanzeige
- 15 Fig. 5 eine schematische Darstellung der Signalformen zur Ansteuerung einer Matrixanzeige gemäss Fig. 4.

Fig. 1 zeigt einen schematischen Querschnitt durch einen Teil einer Flüssigkristallzelle. Die Zelle besteht wie üblich aus zwei im Abstand voneinander angeordneten Trägerplatten 1, 2, zwischen denen eine cholesterische Flüssigkristallschicht 3 angeordnet ist.

Die obere Trägerplatte 1 sei diejenige, durch die der Lichteinfall erfolgt und auf deren Seite sich im Falle einer reflektiv betriebenen Anzeige der Beobachter befindet. Die dem Flüssigkristall zugewandte Oberfläche der Trägerplatte 1 ist so behandelt, dass sie die angrenzenden Flüssigkristallmoleküle homogen orientiert. Diese sogenannte homogene Wandorientierung kann mit den üblichen Methoden erzeugt werden, d.h. also beispielsweise durch Reiben, Schrägbedampfen etc..

Die homogene Wandorientierung der Trägerplatte 1 ist nicht unbedingt für die Funktion der Anzeigezelle erforderlich. Sie dient aber zur Erzielung einer besseren optischen Homogenität, insbesondere im Zustand in dem die Helixachse
5 des Flüssigkristalls senkrecht zu den Trägerplatten steht.

Beide Trägerplatten 1, 2 sind auf den dem Flüssigkristall zugewandten Seiten mit Elektroden versehen, über die die Ansteuerung erfolgt. Diese Elektroden bestehen in bekannter Weise aus dünnen, meistens aufgedampften Schichten von Indiumoxid etc..
10

Da die Anzeige auf dem optischen Unterschied zwischen den beiden Texturen des cholesterischen Flüssigkristalls beruht, muss der Flüssigkristall durch die obere Trägerplatte 1 hindurch sichtbar sein. Das heisst die Trägerplatte 1 muss
15 aus Glas, durchsichtigem Kunststoff etc. bestehen. Auch die obere Elektrode 4 muss durchsichtig sein.



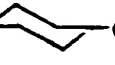















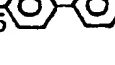

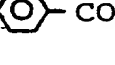
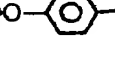
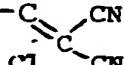

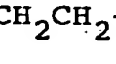
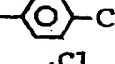
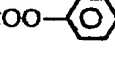
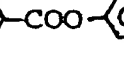
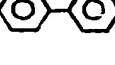

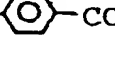
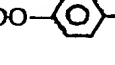

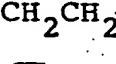
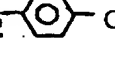
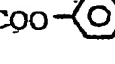



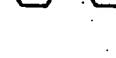

Die untere Trägerplatte soll Licht absorbieren, was üblicherweise dadurch erreicht wird, dass auch die Trägerplatte lichtdurchlässig ist und auf ihrer äusseren Seite
20 eine absorbierende Schicht 6 angebracht ist. Selbstverständlich sind auch andere Konfigurationen denkbar, beispielsweise absorbierende Ausbildung der Elektrode 5 oder der Trägerplatte 2 selbst.

Die Elektroden 4, 5 sind mit einer Ansteuerelektronik
25 verbunden, die für den Zweck dieser Beschreibung lediglich schematisch durch zwei Wechselspannungsquellen 7, 8 mit verschiedenen Frequenzen und einem Schalter 9 dargestellt ist. Für die konkrete und detaillierte Ausbildung der Ansteuerelektronik wird auf die umfangreiche einschlägige Literatur
30 verwiesen, die dem Fachmann bekannt ist.

Die Flüssigkristallschicht 3 besteht aus einer sogenannten Zweifrequenzmischung, wie sie etwa in Appl. Phys. Lett. 41, 697(1982) beschrieben wurde, welcher geeignete

chirale Moleküle zugemischt werden, sodass einerseits die Zweifrequenzeigenschaft erhalten bleibt, andererseits in der Mischung die gefragten cholesterischen Eigenschaften induziert werden, im vorliegenden Fall also das Reflexionsvermögen im sichtbaren Bereich.

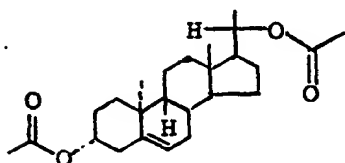
Eine besonders gut geeignete Flüssigkristallmischung setzt sich zum Beispiel wie folgt zusammen: Die nematische Zweifrequenzmischung besteht aus folgenden Komponenten in den angegebenen Gewichtsanteilen:

		Gew. %	
10	C_4H_9  COO  OC_2H_5	9,26 %	} = 2539
	C_4H_9  COO  OC_5H_{11}	13,05 %	
	C_5H_{11}  COO  OCH_3	8,38 %	
	C_5H_{11}  COO  OC_3H_7	10,11 %	
15	C_5H_{11}  CH_2CH_2  OC_2H_5	5,69 %	} = 2545
	C_2H_5   C_3H_7	2,92 %	
	C_5H_{11}   C_3H_7	7,11 %	
	C_5H_{11}   C_3H_7	9,10 %	
	C_7H_{15}   C_3H_7	4,55 %	}
20	C_7H_{15}   COO  COO  	6,14 %	
	C_7H_{15}  CH_2CH_2  COO  COO  	4,39 %	
	C_7H_{15}   COO  COO  CN	3,51 %	
	C_7H_{15}  CH_2CH_2  COO  COO  CN	3,51 %	}
	C_5H_{11}   C_3H_7	8,77 %	
25	C_5H_{11}   CH_2CH_2  C_4H_9	3,51 %	}
		100,00 %	

Diese zwischen -6°C und $+79^{\circ}\text{C}$ nematische Mischung besitzt bei 22°C eine Uebergangsfrequenz f_c von ca. $1,4\text{ kHz}$. Bei Frequenzen $< f_c$ ist die dielektrische Anisotropie positiv, für $f > f_c$ negativ.

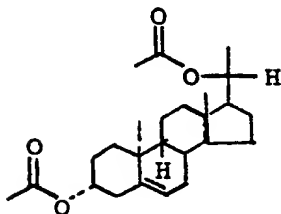
- 5 Zu dieser nematischen Mischung werden folgende chirale Zusätze (in Gew. %) zugefügt, um eine gut sichtbare Farbwirkung im grünen Spektralbereich zu erzielen.

Gew. %

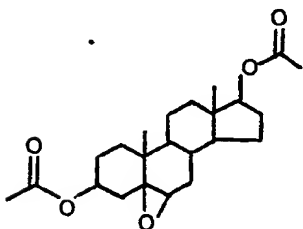


2,0 wt %

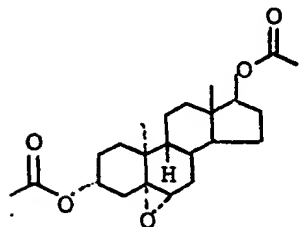
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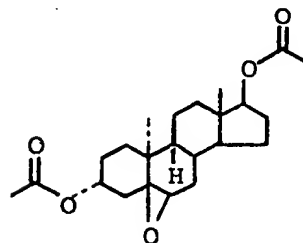
1,7 wt %



2,8 wt %



2,1 wt %



1,9 wt %

Mit der in Figur 1 dargestellten Textur besitzt der Flüssigkristall die für die cholesterische Phase typische schraubenförmig verdrehte Molekülanordnung, wobei die Schraubenachse mehr oder weniger parallel zu den Platten-
5 oberflächen liegt. Dies ist in Fig. 1 durch eine Reihe von auf die Zeichenebene projizierten Molekülen schematisch angedeutet.

Wird der Schalter 9 kurzzeitig mit der Spannungs-
quelle 7 verbunden, so gelangt ein Impuls mit einer Frequenz
10 von mehr als 1,4 kHz, vorzugsweise etwa 10 kHz, an den Flüssigkristall 3, worauf dieser in den Zustand mit platten-
normaler Helixachse übergeht. Dieser Zustand ist in Fig. 2
gezeigt. Bei der in Fig. 2 gezeigten schematischen Dar-
stellung handelt es sich um dieselbe Zelle wie in Fig. 1.
15 Lediglich der Flüssigkristall 3 weist jetzt eine andere Tex-
tur auf, die sich dadurch auszeichnet, dass die ausgebildeten Schraubenwindungen mit ihrer Achse senkrecht auf den Träger-
platten 1, 2 stehen. Die Moleküle sind in diesem Zustand so-
mit im wesentlichen parallel zu den Plattenoberflächen orien-
20 tiert.

Die Textur mit plattennormaler Helixachse bleibt
ebenfalls ohne Energiezufuhr von aussen über lange Zeit hin-
weg unverändert bestehen. Dies ist dadurch angedeutet, dass
auch in Fig. 2 der Schalter 9 geöffnet ist. Wird der Schal-
25 ter 9 so umgelegt, dass die Spannungsquelle 8 mit den
Elektroden verbunden ist, d.h. wird ein Spannungsimpuls mit
einer Frequenz von weniger als 1,4 kHz, d.h. vorzugsweise
etwa 100 Hz zugeführt, so geht der Flüssigkristall wieder
in seine Textur mit plattenparalleler Helixachse über.

30 Die Anzeigezelle besitzt also zwei wirklich stabile
Zustände und kann durch Anlegen von Wechselspannungsimpulsen
mit unterschiedlichen Frequenzen jeweils von einem zum ande-
ren Zustand geschaltet werden. Zur Beibehaltung der beiden
Zustände braucht es keine Haltespannung. Wie die Experimente

ergeben haben sind beide Zustände ohne angelegte Spannung über mehrere Wochen unverändert stabil.

In Versuchszellen wurden die Umschaltvorgänge mittels Rechtecksignalen von 60 Volt RMS durchgeführt. Zu einer
5 10 μm dicken Zelle mit cholesterischer Füllung mit einer Ganghöhe P von $P=0.38 \mu\text{m}$ führte das zu Schaltzeiten von ca. 250 ms für das Schalten in den Zustand mit plattennormaler Helixachse und von ca. 50 ms für den Rückschaltprozess. Bei kleineren Spannungen waren die Schaltzeiten länger, und
10 die Texturänderungen fanden unterhalb gewisser Schwellenwerte kaum mehr statt. Bei Anlegen der Niederfrequenz findet bei ca. doppelter Spannung, d.h. bei 120 V der cholesterisch-nematische Phasenübergang statt. Allerdings befindet man sich dann schon im Bereich hoher Durchschlagsgefahr.

15 Durch Variieren der Spannungen und Modifizieren der Zweifrequenzmischungen dürften noch Verbesserungen der Schaltzeiten erzielbar sein.

Der für eine Anzeige erforderliche optische Kontrast besteht darin, dass in der Textur mit plattenparalleler
20 Helixachse der Flüssigkristall ziemlich gut lichtdurchlässig ist und damit die rückseitige Platte sichtbar ist, die gemäß ihrer absorbierender Eigenschaft dunkel erscheint. Im Zustand mit plattennormaler Helixachse findet dann die erwähnte frequenzselektive Reflexion des Lichts statt. Dies
25 führt dazu, dass von weissem Licht nur bestimmte Anteile zurückgestreut werden und der Flüssigkristall dadurch intensiv farbig erscheint. Die jeweilige Farbe hängt von der Ganghöhe des cholesterischen Flüssigkristalls ab. Da bei den meisten cholesterischen Flüssigkristallen die Ganghöhe tem-
30 peraturabhängig ist ändert sich die Farbe leicht mit wechselnder Temperatur. Es ist jedoch dem Fachmann bekannt, wie dies durch entsprechende Mischungsverhältnisse der Komponenten kompensiert werden kann.

In den Figuren 4 und 5 ist die Verwendung des neuen Effekts in einer Matrixanzeige gezeigt. In dem in Fig. 4 gezeigten Ausschnitt einer Matrixanzeige soll beispielsweise die Fläche Z2/S2 in den Zustand mit plattenparalleler Helix-
5 achse, die Fläche Z2/S4 in den Zustand mit plattennormaler Helixachse gebracht werden. Alle anderen Elemente sollen ihren Zustand unverändert beibehalten!

Die darzustellende Information kann etwa zeilenweise eingelesen werden. Dabei folgen Hoch- und Niederfrequenz-
10 spannungen abwechselungsweise. An der gewählten Zeile Z2 liegt von jeder Frequenz je einmal eine Spannung von zwei Amplitudeneinheiten, während die übrigen Zeilen ohne Spannung bleiben

An den Spalten liegt stets eine Amplitudeneinheit. Für
15 Elemente, die unverändert bleiben sollen, d.h. also in den Spalten S1 und S3 ist sie in Phase mit der Zeilenspannung. Wenn der Zustand eines Elementes neu definiert werden soll, d.h. also in den Spalten S2 und S4 ist die Spannung in Gegenphase zur entsprechenden Zeilenspannung. An den umzu-
20 schaltenden Elementen der Zeile liegen also drei Spannungseinheiten, während an allen übrigen je eine Einheit liegt.

Die Zeiten, während welchen eine Frequenz jeweils anliegt, sind dadurch bestimmt, dass unter drei Spannungseinheiten eine eindeutige Definition des Zustandes eintritt,
25 während unter einer Einheit im Wechsel von Hoch- und Niederfrequenz beide Zustandsmöglichkeiten ungeändert bleiben. Diese Zeiten τ_{NF} , τ_{HF} hängen von Material- und Zellenparametern ab und müssen von Fall zu Fall optimiert werden.

Patentansprüche

1. Flüssigkristallzelle mit einem cholesterischen Flüssigkristall zwischen zwei mit Ansteuerelektroden versehenen Trägerplatten, dadurch gekennzeichnet, dass der Flüssigkristall in zwei optisch verschiedenen stabilen
5 Texturen existiert und eine dielektrische Anisotropie besitzt, die bei Frequenzen unterhalb eines Schwellwerts positiv ist wodurch der Flüssigkristall durch Anlegen einer Wechselspannung mit einer solchen niedrigen Frequenz eine der beiden stabilen Texturen annimmt, bei Frequenzen ober-
10 halb des Schwellwerts negativ ist, wodurch der Flüssigkristall durch Anlegen einer Wechselspannung mit einer höheren Frequenz die andere stabile Textur annimmt.

2. Flüssigkristallzelle nach Anspruch 1, dadurch gekennzeichnet, dass die auf der Einfallsseite des Lichts
15 befindliche Trägerplatte auf ihrer dem Flüssigkristall zugewandten Oberfläche eine Beschaffenheit aufweist, die die Flüssigkristallmoleküle homogen orientiert.

3. Flüssigkristallzelle, nach Anspruch 1, dadurch gekennzeichnet, dass die auf der Einfallsseite des Lichts
20 befindliche Trägerplatte auf ihrer dem Flüssigkristall zugewandten Oberfläche eine Beschaffenheit aufweist, die die Flüssigkristallmoleküle homöotrop orientiert.

4. Flüssigkristallzelle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass der Flüssigkristall
25 in einer der beiden stabilen Texturen eine parallel zu den Trägerplatten, in der anderen stabilen Textur eine senkrecht zu den Trägerplatten liegende Helixachse aufweist.

5. Flüssigkristallzelle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ansteuerelektroden auf einer Trägerplatte in Zeilen-, auf der anderen
30 Trägerplatte in Spaltenleiter unterteilt sind und auf diese

Weise eine Matrixanzeige bilden.

6. Flüssigkristallzelle nach Anspruch 5, dadurch gekennzeichnet, dass die Zeilen- und Spaltenleiter abwechselnd mit einem niederfrequenten und einem hochfrequenten
5 Signal beaufschlagt werden.

7. Flüssigkristallzelle nach Anspruch 6, dadurch gekennzeichnet, dass zum Einlesen einer Zeile an dem anzustuernden Zeilenleiter ein Signal mit einer bestimmten
10 Amplitude und an allen anderen Zeilenleitern kein Signal anliegt, während zugleich allen Spaltenleitern ein Signal zugeführt wird, dessen Amplitude halb so gross ist wie die des Zeilensignals und für die umzuschaltenden Kreuzungspunkte gegenphasig zum Zeilensignal, für alle anderen Kreuzungspunkte mit dem Zeilensignal in Phase ist.

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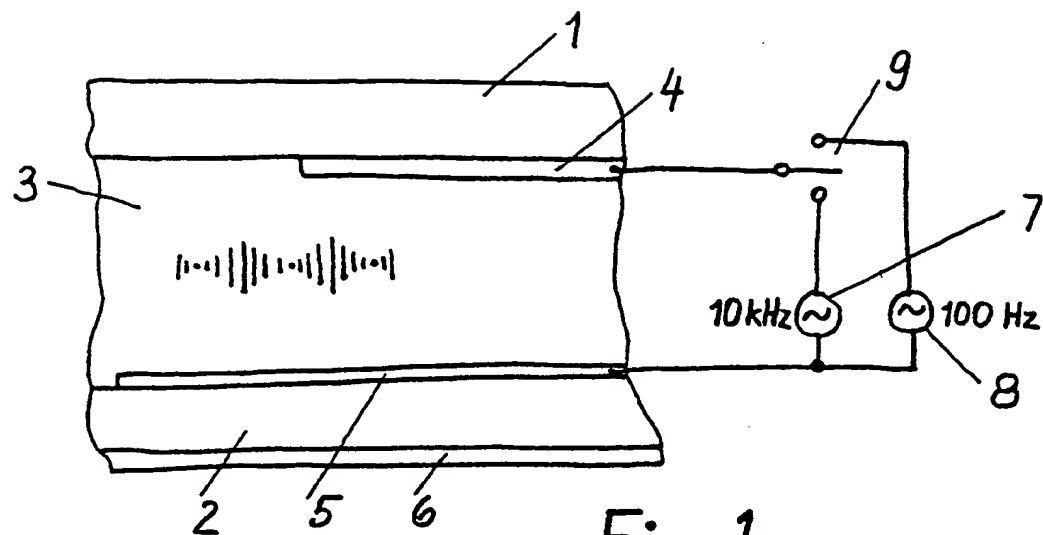
$\frac{1}{2}$ 

Fig. 1

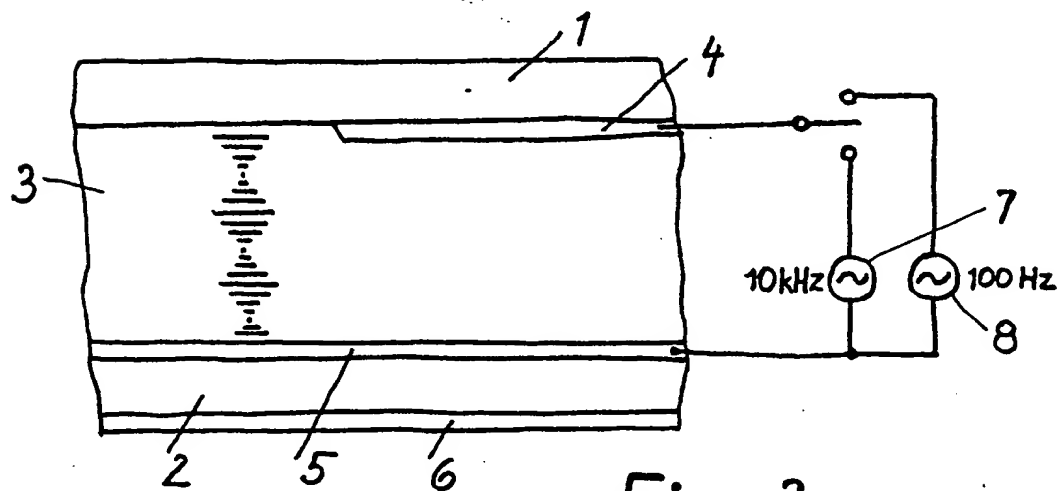


Fig. 2

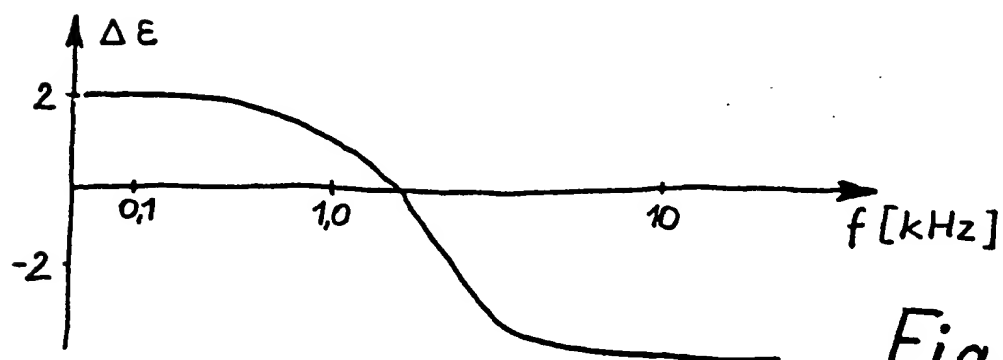


Fig. 3

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2/2

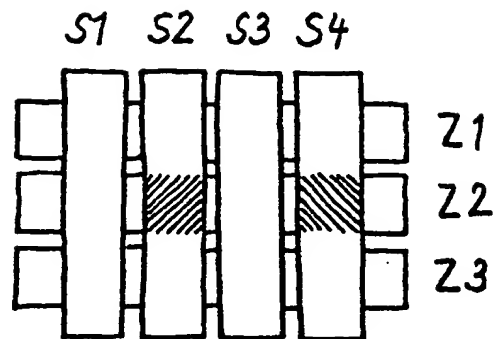


Fig. 4

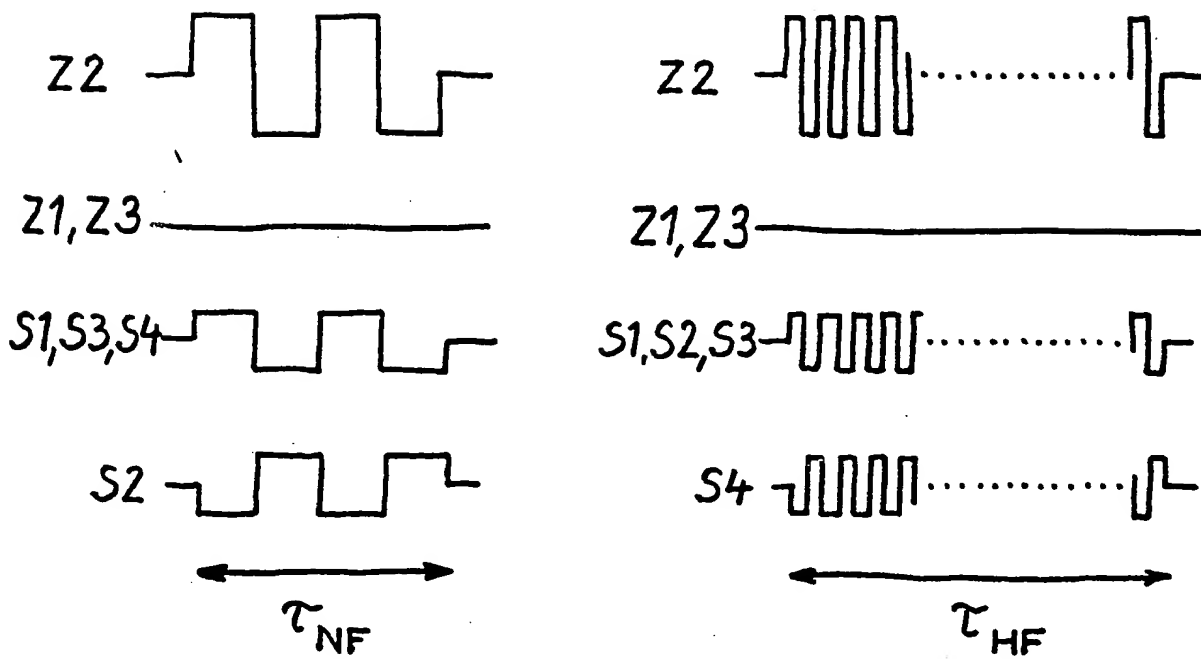


Fig. 5

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C09K 19/52, G02F 1/13	A1	(11) International Publication Number: WO 94/10260 (43) International Publication Date: 11 May 1994 (11.05.94)
(21) International Application Number: PCT/US93/09999 (22) International Filing Date: 19 October 1993 (19.10.93) (30) Priority data: 07/969,093 30 October 1992 (30.10.92) US PCT/US92/09367 30 October 1992 (30.10.92) WO (34) Countries for which the regional or international application was filed: 08/057,662 4 May 1993 (04.05.93) US et al. US (71) Applicant: KENT STATE UNIVERSITY [US/US]; East Main & Lincoln Street, Kent, OH 44242 (US). (72) Inventors: WEST, John ; 5050 Fish Creek Road, Stow, OH 44224 (US). YANG, Deng-Ke ; 826 Allerton Street, Kent, OH 44240 (US).		(74) Agent: SHARPE, Richard, A.; Watts, Hoffmann, Fisher & Heinke Co., 100 Erieview Plaza, Suite 2850, Cleveland, OH 44114-1824 (US). (81) Designated States: CA, JP, KR, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SB). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MULTISTABLE CHIRAL NEMATIC DISPLAYS (57) Abstract <p>A light modulating reflective cell comprising a polymer-free chiral nematic liquid crystalline light modulating material is disclosed. The cell includes nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount effective to form focal conic and twisted planar textures. The chiral material has a pitch length effective to reflect light in the visible spectrum, wherein the focal conic and twisted planar textures are stable in the absence of a field and the liquid crystal material is capable of changing textures upon the application of a field.</p>		

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MULTISTABLE CHIRAL NEMATIC DISPLAYS

5 This application was made in part with Government support under cooperative agreement number DMR 89-20147 awarded by the National Science Foundation. The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

Related Applications

10 This application is a continuation in part of U.S. Serial No. 07/694,840 filed May 2, 1991, incorporated herein by reference, U.S. Serial No. 07/885,154, filed May 18, 1992, incorporated herein by reference and U.S. Serial No. 07/969,093, incorporated herein by reference.

Technical Field

15 The present invention relates generally to liquid crystalline light modulating devices, and more specifically to new polymer free liquid crystalline display cells and materials which exhibit different optical states under different electrical field conditions and are characterized by a unique combination of properties, including optical multistability and haze-free light transmission at all
20 viewing angles in both a field-ON or field-OFF mode.

Electrically switchable liquid crystal films intended for use in electro-optical devices have been prepared using various types and concentrations of liquid crystal and polymer. One such technique involves imbibing liquid crystal into micropores of a plastic or glass sheet. Another technique involves
25 evaporation of water from an aqueous emulsion of nematic liquid crystal in a solution of water-soluble polymer such as polyvinyl alcohol or in a latex emulsion.

30 A different procedure offering significant advantages over mechanical entrapment techniques and the emulsification procedure involves phase separation of liquid crystal from a homogeneous solution with a suitable

synthetic resin to form a liquid crystal phase interspersed with a polymer phase. These types of films, some of which are referred to as PDLC, have been shown to be useful in many applications ranging from large area displays and switchable coatings for windows to projection displays and high-definition television.

All of the above-noted materials and procedures have the disadvantage of requiring numerous and expensive reagents and starting materials. The various imbibing, emulsification or polymerization procedures associated with these systems significantly add to the cost and complexity of their manufacture. Moreover, when significant amounts of polymer are used, they begin to exhibit the characteristic drawback of "haze" at increasing oblique viewing angles until an essentially opaque appearance is detected at an oblique enough angle due to the perceived mismatch between the effective index of refraction of the liquid crystal and the refractive index of the polymer.

In the parent application it was found that good color reflective displays could be prepared using chiral nematic liquid crystal and polymer. These displays had the advantages of exhibiting multiple stable color reflecting states and, when the amount of polymer was low, haze free viewing. However, in spite of their many advantages, these displays still require the use of polymers and hence, have the drawbacks associated therewith.

Surprisingly, it has now been discovered that a polymer free multistable color reflecting cell can be prepared that exhibits stable color reflecting and light scattering states with multiple stable optical states therebetween characterized by varying degrees of intensity of reflection. Depending upon the voltage of the electric field addressing pulse, the material can be switched between these multiple optical states, all of which are stable in the absence of an applied field.

DISCLOSURE OF THE INVENTION

An important feature of the invention is that a reflective color display cell can be prepared without polymer so that it exhibits multiple optically different states, all of which are stable in the absence of an applied field. The

display can be driven from one state to another by an electric field.

Depending upon the magnitude and shape of the electric field pulse, the optical state of the material can be changed to a new stable state which reflects any desired intensity of colored light along a continuum of such states, thus providing a stable "grey scale." Surprisingly, these materials can be prepared without the need for polymers and the added expense and manufacturing complexities associated therewith.

Generally, a sufficiently low electric field pulse applied to the material results in a light scattering state which is white in appearance. In this state, a proportion of the liquid crystal molecules have a focal conic texture as a result of competition between any surface effects, elastic forces and the electric field. After application of a sufficiently high electric field pulse, i.e., an electric field high enough to homeotropically align the liquid crystal directors, the material relaxes to a light reflecting state that can be made to appear as green, red, blue, or any pre-selected color depending upon the pitch length of the chiral nematic liquid crystal. The light scattering and light reflecting states remain stable at zero field. By subjecting the material to an electric field in between that which will switch it from the reflecting state to the scattering state, or vice versa, one obtains stable grey scale states characterized by varying degrees of reflection in between that exhibited by the reflecting and scattering states. When the chiral nematic liquid crystal is in a planar colored light reflecting texture and an intermediate electric field pulse is applied, the amount of material in the planar texture, and the intensity of reflectivity of the colored light, decrease. Similarly, when the material is in the focal conic texture and an intermediate electric field pulse is applied, the amount of material in the planar texture will increase as will the intensity of reflection from the cell. When the electric field is removed, the material is stable and remains in the established texture to reflect that intensity of light indefinitely, regardless of which texture it started from.

If an electric field high enough to homeotropically align the liquid crystal directors is maintained, the material is transparent until the field is removed. When the field is turned off quickly, the material reforms to the

light reflecting state and, when the field is turned off slowly, the material reforms to the light scattering state. In each case, the electric field pulse is preferably an AC pulse, and more preferably a square AC pulse, since a DC pulse will tend to cause ionic conduction and limit the life of the cell.

5 While not wanting to be bound by theory, it is believed that when the voltage is applied, a proportion of the material enters a turbid phase while the field is on. Those portions of the material that exhibit the turbid phase tend to relax to a focal conic, light scattering texture upon removal of the field. Those portions of the material unaffected by the field, i.e., those portions that do not enter the turbid phase, remain in the planar, light reflecting texture. The amount of light reflected from the cell depends on the amount of material in the planar reflecting texture. When the voltage of the electric field is increased, a higher proportion of the material enters the turbid phase while the field is on, followed by relaxation to the focal conic texture when the field is removed. Since the reflection from the cell is proportional to the amount of material in the planar reflecting texture, reflection from the cell decreases along a grey scale as a result of an increase in the magnitude of the field because more of the material enters the turbid phase and is switched to the focal conic texture. At a certain threshold voltage, which depends upon the material, substantially all of the material is switched to the focal conic texture upon removal of the field, characterized by a light scattering condition where the reflectivity of the cell is at or near a minimum. When the voltage is removed, the assumed texture is stable and will remain scattering indefinitely. When the voltage is increased further, to a point high enough to untwist the liquid crystal and homeotropically align the liquid crystal directors, the material is transparent and will remain transparent until the voltage is removed. From the homeotropic texture, the material tends to relax to the stable color reflecting planar texture upon removal of the field.

30 When the material is in a light scattering focal conic texture and a low voltage pulse is applied, the material begins to change texture and again stable grey scale reflectivities are obtained. Since the material here starts in the scattering focal conic texture, the grey scale reflectivities are characterized by

an increase in the reflectivity from that exhibited when substantially all of the material is in the scattering focal conic texture, although it has been observed that the reflectivity may initially decrease in some samples. The increase in reflectivity is believed to be attributable to proportions of the material that become homeotropically aligned as a result of the applied field. Those proportions that are homeotropically aligned relax to a stable planar light reflecting texture upon removal of the field, while the remainder of the material exhibits the turbid phase as a result of the field and relaxes back to the focal conic texture upon removal thereof. When the voltage is increased still further, to the point of homeotropically aligning substantially all of the liquid crystal, the material again appears clear and relaxes to the stable planar color reflecting texture upon removal of the field.

In short, it is believed that those proportions of the material that enter the turbid phase as the result of an applied field relax to a stable focal conic texture upon removal of the field, and those portions that become homeotropically aligned due to the application of an applied field relax to a stable planar texture upon removal of the field. It is believed that the material returns to the scattering focal conic state when a high electric field is slowly removed from the homeotropically aligned liquid crystal because slow removal takes the material into the turbid phase from which it seems to consistently relax to a focal conic texture after removal of a field. When a high field is removed quickly, the material does not enter the turbid phase and thus, relaxes to the planar reflecting texture. In any case, it can be seen that electric field pulses of various magnitudes below that necessary to drive the material from the stable reflecting state to the stable scattering state, or vice versa, will drive the material to intermediate states that are themselves stable. These multiple stable states indefinitely reflect colored light of an intensity between that reflected by the reflecting and scattering states. Thus, depending upon the magnitude of the electric field pulse the material exhibits stable grey scale reflectivity without the need for polymer. The magnitude of the field necessary to drive the material between various states will, of course, vary depending upon the nature and amount of the particular liquid crystal and thickness of

the cell. Application of mechanical stress to the material can also be used to drive the material from a light scattering to a light reflecting state.

A major advantage of the multistable material is that it does not require an active matrix to make a high-definition flat panel screen. The screen can be prepared without active elements at each pixel site and a multiplexing scheme used to address the display. This greatly simplifies production, increases yield and reduces the cost of the display. Since the material does not require polymer, even greater simplification of production and cost savings are realized by the invention. Other advantages of the present invention are that the light scattering and light reflecting states are stable without requiring polymer or delicate surface conditions of the substrate. Display devices made with the material of the invention do not require polarizers which limit the brightness of the displays and color is introduced by the material itself without the need of color filters which also can reduce brightness.

The advantageous properties described above are achieved in the invention by providing a light modulating reflective cell comprising a polymer free chiral nematic liquid crystalline light modulating material, including nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount effective to form focal conic and twisted planar textures having a pitch length effective to reflect light in the visible spectrum, wherein the focal conic and twisted planar textures are stable in the absence of a field and the liquid crystal material is capable of changing textures upon the application of a field.

The addressing means can be of any type known in the art, such as an active matrix, a multiplexing circuit, electrodes and lasers. As a result, the new material can be made to exhibit different optical states, i.e., light transmitting, light scattering, light reflecting and stable grey scale in between these states, under different field conditions without the need for polymer and the complicated manufacturing processes associated therewith.

The chiral nematic liquid crystal is a mixture of nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount sufficient to produce a desired pitch length. Suitable nematic liquid crystals and chiral

materials are commercially available and would be known to those of ordinary skill in the art in view of this disclosure. The amount of nematic liquid crystal and chiral material will vary depending upon the particular liquid crystal and chiral material used, as well as the desired mode of operation.

5 The wavelength of the light that is reflected by the material is given by the relation $\lambda=np$, where n is the average refractive index and p is the pitch length. Wavelengths between about 350 nm and 850 nm are in the visible spectrum. Accordingly, one of ordinary skill in the art will be able to select appropriate materials for the invention based upon the refractive indices of the materials involved and on general principles of chiral doping of liquid crystals to obtain optimum pitches, for example, the procedures taught in the manual distributed by Hoffmann-La Roche, Ltd., entitled How to Dope Liquid Crystal Mixtures in Order to Ensure Optimum Pitch and to Compensate the Temperature Dependence, Schadt et al., (1990), incorporated herein by reference.

10 In a preferred embodiment the pitch length of the chiral nematic liquid crystal is in a range of from about .25 to about 1.5 microns, more preferably from about .45 to about .8 microns. Typical pitch lengths are 0.27 microns for blue color, 0.31 microns for green color and 0.40 microns for red color. Moreover, the chiral nematic liquid crystal preferably contains from about 20 to about 60% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material and, still more preferably, from about 20 to about 40% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material. The ranges can vary, however, depending upon the chiral material and liquid crystal. The nematic liquid crystal preferably has a positive dielectric anisotropy of at least about 5 and more preferably at least about 10. It will be understood that the weight amounts can vary depending upon the particular liquid crystal and chiral material used.

25 In carrying out the invention, the solution containing the desired amounts of nematic liquid crystal and chiral material is prepared and introduced between cell substrates, at least one of which is transparent. The cell is then sealed around its edges with, for example, epoxy or other materials

30

known in the art. The cell can be filled by methods known to those of ordinary skill in the art, such as by capillary action. A preferred technique is to vacuum fill the cells. This improves cell uniformity and eliminates bubbles in the cell. For electrically addressable cells the cell walls are coated with transparent electrodes, such as indium tin oxide, prior to the introduction of the liquid crystal.

While not necessary to the invention, in some instances it is desirable to treat the cell walls with materials in addition to the electrodes, such as detergent or chemicals, to obtain variations in the contrast or switching characteristics. These treatments can be used to affect the uniformity of the liquid crystal, alter the stability of the various textures and to alter the strength of any surface anchoring. In addition to using a wide variety of materials for such surface treatments, the treatments on opposite substrates may differ. For example, the substrates may be rubbed in different directions, one substrate may include the additional treatment while the other substrate does not, or opposite substrates may be treated with different materials. As noted above, such additional treatments can have the effect of altering the characteristics of the cell response.

Optionally, other additives may be included in the chiral nematic liquid crystal mixture to alter the characteristics of the cell. For example, while color is introduced by the liquid crystal material itself, pleochroic dyes may be added to intensify or vary the color reflected by the cell. Similarly, additives such as fumed silica can be dissolved in the liquid crystal mixture to adjust the stability of the various cholesteric textures.

The invention also features an improved method of addressing a polymer free chiral nematic liquid crystal material capable of being switched between a color reflecting state that reflects a maximum reference intensity, and a light scattering state exhibiting a minimum reference intensity. The improvement comprises applying voltage pulses of varying magnitude sufficient to achieve color reflectivity between said maximum and minimum, thereby producing stable grey scale reflectance from the material.

Preferably the method is characterized by subjecting the material to an AC pulse of sufficient duration and voltage to cause a proportion of said chiral nematic material to exhibit a first optical state and the remaining proportion of the chiral nematic material to exhibit a second optical state that is different than the first state. In the preferred embodiment, the proportion of the material in the first optical state exhibits the planar texture and the remainder of the material in the second optical state exhibits the focal conic texture, the intensity of reflection being proportional to the amount of the material in the planar reflecting texture.

Many additional features, advantages and a fuller understanding of the invention will be had from the following detailed description of preferred embodiments and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagrammatic, cross-sectional illustration of a light modulating cell incorporating the liquid crystalline material of the invention.

Figure 2 is a diagrammatic, fragmentary, enlarged cross-sectional illustration of the material when the liquid crystal is homeotropically aligned to affect an optically clear state.

Figure 3 is a diagrammatic, fragmentary, enlarged cross-sectional illustration of the material in a light scattering state.

Figure 4 is a diagrammatic, fragmentary, enlarged cross-sectional illustration of the material when the liquid crystal has a twisted planar texture.

Figure 5 is a plot of the electro-optic response of a cell to AC pulses of varying voltages demonstrating grey scale reflection in the voltage range of about 30 and 140 volts starting from the planar texture, and between about 140 and 180 starting from the focal conic.

DESCRIPTION OF PREFERRED EMBODIMENTS

The diagrammatically illustrated cell in Figure 1 comprises glass plates 10, 11 which are sealed around their edges and separated by spacers 12. As shown, the glass plates 10, 11 are coated with indium-tin oxide (ITO) or the

like to form transparent electrodes 13. The reference character 14 represents an optional surface coating which can be applied to the electrodes in order to affect the liquid crystal directors, or to alter the contrast, reflection or switching characteristics of the cell. The opposite coatings 14 may be the same material or different material, may be rubbed in different directions, or one or both of the coatings 14 may be eliminated altogether.

The cell of Figure 1 is filled with the polymer free liquid crystalline material of the invention. The liquid crystalline light modulating material is generally comprised of chiral nematic liquid crystal 16 having nematic liquid crystal with positive dielectric anisotropy and chiral material. An AC voltage source 17 is shown connected to the electrodes 13 in order to switch the cell between different optical states.

It is to be understood that the form of the cell depicted in Figure 1 has been chosen only for the purpose of describing a particular embodiment and function of the polymer free liquid crystalline material of the invention, and that the material can be addressed in various ways and incorporated in other types of cells. For example, instead of being addressed by externally activated electrodes, the material can be addressed by an active matrix, a multiplexing scheme or other type of circuitry, all of which will be evident to those working in the art. Similarly, the cells can be prepared without the optional surface treatment layers 14.

When the optional surface treatment layers are employed in addition to rubbed or unrubbed ITO or other suitable electrodes for the purpose of altering the characteristics of the cell, a wide variety of materials may be used. Suitable materials include polymethylmethacrylate (PMMA), unrubbed polyimide, polyisobutylmethacrylate, poly-n-butylmethacrylate, polyvinylformal (PVF) and polycarbonate. Both plates may have the same or different materials and may be rubbed, unrubbed or otherwise textured. Similarly, opposite surfaces may be rubbed in different directions or textured in different manners. Best results are obtained with rubbed ITO without any additional surface treatments.

5 The liquid crystal material comprises a nematic liquid crystal having positive dielectric anisotropy and a chiral material, e.g., cholesteric liquid crystal, but does not contain any polymer. Suitable nematic liquid crystals include, for example, E7, E48, E31 and E80 manufactured by E. Merck, although virtually any cyanobiphenyl known in the art having suitable positive anisotropy will likely suffice. Suitable chiral agents include, for example, CB15, CE2 and TM74A, also manufacture by E. Merck. Other nematic liquid crystals and chiral materials suitable for use in the invention would be known to the skilled artisan in view of the instant disclosure. Other optional components that may be added to the chiral nematic liquid crystal mixture include, for example, fumed silica to adjust the stability of the various textures and dyes to adjust the color.

10 In a preferred manner of preparing the cell shown in Figure 1, a solution of the chiral nematic liquid crystal together with any additional dyes or additives and the like is prepared. The solution is then introduced between the glass plates 10, 11, shown here having the optional coatings 14. This can be done by methods known to those of ordinary skill in the art, such as capillary filling and, more preferably, vacuum filling. Once introduced between the plates the cell is sealed around its edges as is known in the art.

15 Polymer free displays prepared according to the invention capable of being switched between stable planar, focal conic and grey scale states are shown in the following non-limiting examples.

Example 1

20 A chiral nematic liquid crystal mixture containing 37.5% by weight E48 (nematic liquid crystal from EM Chemicals) and 62.5% by weight TM74A (chiral additive from EM Chemicals) was prepared. A one inch square cell was then formed from two substrates coated with ITO. The ITO coatings of both substrates were buffed parallel to each other. 10 μ m glass spacers were sprayed onto one substrate and the second substrate was sandwiched so that two of its edges overlapped the first substrate and the cell held together with

25
30

clamps. Five minute epoxy (Devcon) was then used to seal the two non-overlapping edges.

The cell was held vertically and a bead of the chiral nematic liquid crystal was placed along the top open edge of the cell. The cell then filled spontaneously by capillary action over a period of approximately 15 minutes. Once filled, the residual liquid crystal mixture is removed from the edge and the open edges sealed with five minute epoxy.

The cell was initially in the planar reflecting state. A 100ms lower voltage pulse of about 115 volts and 1 KHz, switched the cell into the focal conic scattering state. A 100 ms higher voltage pulse of about 180 volts, and 1KHz switched the cell back to the planar reflecting state. Both the planar and focal conic states were stable in the absence of a field and the cell exhibited multiple stable grey scale reflecting states between the scattering and reflecting states.

Example 2

A mixture of E48 and TM74A in a weight ratio of 0.6:1 was introduced between ITO coated glass substrates spaced 10 micrometers apart as in the previous example. The substrates were additionally coated with an unrubbed polyimide layer. The cell was initially in the focal conic, scattering texture that transmitted only about 30% of an HeNe beam through the cell. A 10 ms, 155 volt, 1 KHz Ac pulse switched the cell to a planar texture reflecting green colored light. The transmission from the cell in the reflecting state was about 65%. A 95 volt pulse of the same duration and wavelength switched the cell back to the focal conic, scattering state. The cell switched between states in less than 10ms.

Example 3

A cell was prepared as in the preceding examples with a mixture of CB15, CE2 (chiral materials from EM Chemicals) and E48 nematic liquid crystal in a weight ratio of 0.15:0.15:0.7. In this cell the driving voltage was cut approximately in half because the dielectric anisotropy of the mixture was

higher than when TM74A was used. The electro-optic response of this material was similar to that of example 1.

Table I shows numerous additional examples of materials prepared according to the preceding examples. The concentration of chiral material, and the type and concentration of nematic liquid crystal were varied in these cells. In each case the chiral material was a 50:50 mixture of CE2 and CB15. Each cell employed unrubbed ITO electrodes as the only surface treatment on the substrates. The materials in Table I all exhibited multistability in the visible spectrum, i.e., stable reflecting, scattering and grey scale states.

Table I

<u>Chiral Agent</u>	<u>Nematic LC</u>	<u>Thickness</u>	<u>Color</u>	<u>Multistability</u>	<u>Surface</u>
4. CE2/CB15 30%	E48 70%	10 μm	Red	Yes	ITO
5. CE2/CB15 40%	E48 60%	10 μm	Grn	Yes	ITO
6. CE2/CB15 50%	E48 50%	10 μm	Blu	Yes	ITO
7. CE2/CB15 30%	E7 70%	10 μm	Red	Yes	ITO
8. CE2/CB15 40%	E7 60%	10 μm	Grn	Yes	ITO
9. CE2/CB15 30%	E31 70%	10 μm	Red	Yes	ITO
10. CE2/CB15 40%	E31 60%	10 μm	Grn	Yes	ITO

Table II shows examples of materials prepared according to the preceding examples exhibiting multistability with varying surface treatment materials and cell thicknesses. In each case the nematic liquid crystal was E31 (EM Chemicals) in an amount of 60% by weight based on the combined weight of nematic liquid crystal and chiral material. The chiral material in each case was a 50:50 mixture of CE2 and CB15 (EM Chemicals) present in an amount of 40% by weight based on the weight of chiral material and nematic liquid crystal. Each cell exhibited a green reflecting state. The reflecting and scattering states were stable in the absence of a field and the cells exhibited stable grey scale states therebetween. In examples 17 and 18, the PVF coatings on opposite substrates were rubbed parallel and perpendicular to each other, respectively. Similarly, the coatings on opposite substrates in examples 22 and 23 were rubbed parallel and perpendicular to

each other, respectively. The coatings in examples 21 and 24 were simply unrubbed ITO electrodes, and in the case of example 25, the ITO coatings on opposite substrates were rubbed parallel to each other. The i-butyl and n-butyl in examples 13-15 stand for n-butyl and i-butyl methacrylate, respectively. The spacing in these examples was adjusted by glass spheres as in the preceding examples.

Table II

	<u>Surface</u>	<u>Thickness</u>	<u>Multistability</u>
10	11. 100% n-Butyl	10 μm	yes
	12. 100% i-Butyl	10 μm	yes
	13. 75% i-Butyl/25% n-Butyl	10 μm	yes
	14. 25% i-Butyl/75% n-Butyl	10 μm	yes
	15. 50% i-Butyl/50% n-Butyl	10 μm	yes
15	16. polyvinyl formal (PVF)	5 μm	yes
	17. PVF rubbed parallel	5 μm	yes
	18. PVF rubbed perpendicular	5 μm	yes
	19. polymethylmethacrylate (PMMA)	5 μm	yes
	20. polycarbonate (PCBR)	5 μm	yes
20	21. ITO	6.7 μm	yes
	22. PI rubbed parallel	6.7 μm	yes
	23. PI rubbed perpendicular	6.7 μm	yes
	24. ITO	10 μm	yes
	25. ITO rubbed	10 μm	yes

Table III is analogous to Table II in that it provides additional examples of multistable materials obtained as in example 1 with varying surface treatments and cell thicknesses. However, the materials in Table III consisted of TM74A chiral material in an amount of 60% by weight based on the weight of the chiral material and nematic liquid crystal. The nematic liquid crystal was E48 present in an amount of 40% by weight. These cells also reflected green colored light in the planar light reflecting texture and exhibited multistability as in the preceding examples.

Table III

	<u>Surface</u>	<u>Thickness</u>	<u>Multistability</u>
5	26. 100% n-Butyl	10 μm	yes
	27. 100% i-Butyl	10 μm	yes
	28. 75% i-Butyl/25% n-Butyl	10 μm	yes
	29. 25% i-Butyl/75% n-Butyl	10 μm	yes
	30. 50% i-Butyl/50% n-Butyl	10 μm	yes
10	31. polymethylmethacrylate (PMMA)	5 μm	yes
	32. PMMA rubbed parallel	5 μm	yes
	33. PMMA rubbed perpendicular	5 μm	yes
	34. polycarbonate (PCBR)	5 μm	yes
	35. PCBR rubbed parallel	5 μm	yes
	36. PCBR rubbed perpendicular	5 μm	yes
15	37. PI	10 μm	yes
	38. ITO	10 μm	yes
	39. ITO rubbed	10 μm	yes

20 The polymer free multistable color display cells of the invention exhibit
 a stable grey scale phenomenon characterized by the ability of the material to
 reflect indefinitely any selected intensity of light between the intensity reflected
 by the reflecting state and that reflected by the scattering state, the former
 being when substantially all of the material exhibits the planar texture and the
 later being when substantially all of the material exhibits the focal conic
 25 texture. For purposes of this invention, the reflecting state reflects colored
 light at a maximum intensity for a given material, the color of the reflected
 light being determined by the pitch length of the chiral material. An electric
 field pulse of an appropriate threshold voltage will cause at least a portion of
 the material to change its optical state and the intensity of reflectivity to
 30 decrease. If the AC pulse is high enough, but still below that which will
 homeotropically align the liquid crystal, the optical state of the material will
 change completely to the scattering state which reflects light at a minimum
 intensity for a given material. In between the reflecting state, which for a given
 material can be considered to define the maximum intensity of reflectivity for
 35 that material, and the scattering state, which can be considered to define the
 minimum intensity of reflectivity, the intensity of reflectivity ranges along a grey
 scale, which is simply a continuum of intensity values between that exhibited by

the reflecting and scattering states. By pulsing the material with an AC pulse of a voltage in between that which will convert the material from the reflecting state to the scattering state, or visa versa, one obtains an intensity of reflectivity in this grey scale range.

5 While not wanting to be bound by theory, it has been observed that the intensity of reflectivity along the grey scale when the material begins in the planar texture is approximately linearly proportional to the voltage of the pulse. By varying the voltage of the pulse the intensity of reflectivity of a given color can be varied proportionally. When the electric field is removed the
10 material will reflect that intensity indefinitely. It is believed that pulses within this grey scale voltage range cause a proportion of the material to convert from the planar texture characteristic of the reflecting state, to the focal conic texture characteristic of the scattering state. The intensity of reflectivity along the grey scale is proportional to the amount of chiral material switched from
15 the planar texture to the focal conic texture, or vise versa, which is in turn proportional to the voltage of the AC pulse.

 Figure 4 conceptually illustrates the polymer free multistable material of the invention in its light reflecting state. In this state, the chiral liquid crystal molecules 40 are oriented in a twisted planar structure parallel to the cell
20 walls. Because of the twisted planar texture the material will reflect light, the color of which depends upon the particular pitch length. In this stable reflecting state, the material exhibits maximum reflectivity that constitutes a maximum reference intensity below which the grey scale intensities are observed. The planar texture of the liquid crystal is stable without the
25 presence of polymer. As conceptually illustrated in Figure 3, the multistable color display material is in its light scattering state. In this stable scattering state the material exhibits its minimum intensity of reflection (i.e., maximum scattering) which defines a minimum reference intensity of reflectivity above which the grey scale intensities are observed.

30 Both the light reflecting state of Figure 4 and the light scattering state of Figure 3, as well as the grey scale states therebetween, are stable in the absence of an electric field. If the material is in the light reflecting state of

Figure 4 and a low electric field pulse is applied, the material will be driven to the light scattering state of Figure 3 and will remain in that state at zero field. If the multistable material is in the light scattering state of Figure 3 and a higher electric field pulse sufficient to untwist the chiral molecules is applied, the liquid crystal molecules will reform to the light reflecting state of Figure 4 at the end of the pulse and will remain in that condition. It is to be understood that the voltages per micron of cell thickness necessary to drive the material between optical states may vary depending on the composition of the material, but that the determination of necessary voltages is well within the skill in the art in view of the instant disclosure.

If the high electric field necessary to untwist the liquid crystal molecules is maintained, the liquid crystal directors will be homeotropically aligned so that the material is transparent. If the field is slowly removed, the liquid crystal orientation will reform to the light scattering state of Figure 3, presumably because slow removal allows a significant proportion of the material to enter the turbid phase. When the field is quickly removed, the orientation will reform to the light reflecting state of Figure 4. The intensities of reflectivity reflected between the reflecting state of Figure 4 and the scattering state of Figure 3 are stable grey scale reflectivities. Of course, the intensity value of the reflecting and scattering states may vary as the composition of the material varies, but the grey scale is defined by the range of intensities therebetween.

At voltages less than that which will transform the material from the reflecting state of Fig. 4 to the scattering state of Fig. 3, grey scale states which are themselves stable at zero field are obtained. The reflection from the material in these grey scale states is stable because a proportion of the material is in the planer reflecting texture of Fig. 4 and a proportion of the material is in the focal conic scattering texture of Fig. 3, both of which are stable in the absence of a field.

Thus, for example, if the material is in the reflecting state of Fig. 4 and an electric field pulse is applied having a voltage insufficient to drive all of the liquid crystal 16 into the focal conic texture shown at 50 in Figure 3, i.e.,

insufficient to drive the material completely to the scattering state, the material will reflect colored light of an intensity that is proportional to the amount of material that remains in the planar reflecting texture. The reflectivity will thus be lower than that reflected from the material when all of the chiral nematic liquid crystal is in the planar reflecting texture, but still higher than when switched completely to the focal conic scattering texture. As the voltage of the electric field pulse is increased, more of the chiral material is switched from the planar reflecting texture to the scattering focal conic texture and the reflectivity decreases further until the voltage of the pulse is increased to the point where all or most of the material enters the turbid phase from which it relaxes and is completely switched to the scattering state. If the voltage of the pulse is increased still further, the intensity of reflection begins to increase again until the magnitude of the pulse is sufficient to untwist most of the chiral molecules so that they will again reform to the planar light reflecting texture when the pulse is quickly removed and the material is again in the light reflecting state of Figure 4.

If the material is in the focal conic scattering state of Figure 5, an applied electric field pulse will have a much less dramatic effect on the reflectivity of the cell than when it starts in the planar texture, until the voltage reaches a magnitude sufficient to untwist the chiral material, whereby it will reform to the light reflecting state of Figure 4, as described above, when the field is removed. Grey scale when the material starts in the focal conic texture appears to result when a proportion of the molecules untwist and homeotropically align as a result of the application of the field. This proportion of molecules then relaxes to the planar reflecting texture upon removal of the field.

The response of a cell as described above is illustrated in Figure 6, which shows the response of the material prepared in Example 1 to varying pulse voltages.

The reflectivity of the cell in response to AC pulse of varying voltages was measured. In the measurement, 100 millisecond, 1 KHz AC pulses were used. For this material an applied pulse above about 180V switched the cell

into the reflecting state independent of whether the cell was in the scattering or reflecting state prior to the pulse. Maximum reflection, i.e., transmission, is observed here. The material exhibited maximum scattering when a voltage in the 130 to 140V range was applied, regardless of whether the material was in the planar or focal conic texture prior to the pulse.

The grey scale response of the cell in response to pulses of varying voltage is also seen in Fig. 6. Here the voltage of the pulse was varied and the reflection (% transmission) from the cell was measured. Curve A is the response of the cell when the material is in the reflecting state prior to each pulse. Prior to each pulse plotted on curve A the material was subjected to a high AC pulse to ensure that it was completely in the reflecting state prior to the pulse. When the voltage of the pulse is below about 30V, the reflection of the cell is not significantly affected. When the voltage of the pulse is between about 40V and 110V, the reflectivity of the cell decreases approximately linearly as the voltage of the pulse is increased. Grey scale reflectivity is observed in this voltage range. In each case the material continued to reflect after the pulse was removed. When the voltage of the pulse was increased to from about 120 to 130V, the material was in the scattering state and exhibited near maximum scattering. When the magnitude of the pulse was increased still further, above about 150 to 160V, the reflectivity of the cell increased until the reflectivity approximated its original value, i.e., that of the reflecting state, above 180V.

Curve B shows the response of the cell when the material was initially in the focal conic scattering state prior to the AC pulse. Here the reflectivity of the cell does not significantly change for AC pulses below about 30V. Between about 50 and 150V the scattering actually increases slightly and maximum scattering is observed from the cell. Above about 160V the transmission quickly increased and the cell switched to the reflecting state approximating the maximum transmission above about 180V.

It can be seen that the linear relationship of the grey scale to voltage is much more pronounced, and the grey scale more gradual, when the material starts from the planar texture. Accordingly, most practical applications of the

grey scale phenomenon will likely employ the material starting from the planar texture.

Many modifications and variations of the invention will be apparent to those of ordinary skill in the art in light of the foregoing disclosure. Therefore, it is to be understood that, within the scope of the appended claims, the invention can be practiced otherwise than has been specifically shown and described.

CLAIMS

WHAT IS CLAIMED:

1. A light modulating reflective cell comprising a polymer-free chiral nematic liquid crystalline light modulating material, including nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount effective to form focal conic and twisted planar textures, said chiral material
5 having a pitch length effective to reflect light in the visible spectrum, wherein said focal conic and twisted planar textures are stable in the absence of a field and the liquid crystal material is capable of changing textures upon the application of a field.
2. The cell as claimed in Claim 1 wherein the pitch length of the chiral nematic liquid crystal is in a range of from about .25 to about 1.5 microns.
3. The cell as claimed in Claim 1 wherein the pitch length of the chiral nematic liquid crystal is in a range of from about .45 to about .8 microns.
4. The cell as claimed in Claim 1 wherein the nematic liquid crystal has a positive dielectric anisotropy of at least about 5.
5. The cell as claimed in Claim 1 wherein the nematic liquid crystal has a positive dielectric anisotropy of at least about 10.
6. The cell as claimed in Claim 1 wherein the chiral nematic liquid crystal contains from about 20 to about 60% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material.
7. The cell as claimed in Claim 1 wherein the chiral nematic liquid crystal contains from about 20 to about 40% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material.

8. The cell as claimed in Claim 1 wherein the liquid crystal exhibits a stable light reflecting twisted planar structure in a field-OFF condition following removal of a high field-ON condition, and a stable light scattering focal conic texture in a field-OFF condition following removal of a low field-
5 ON condition.

9. A method of addressing a light modulating cell comprising a polymer free chiral nematic liquid crystalline light modulating material, including nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount effective to form focal conic and twisted planar textures,
5 said chiral material having a pitch length effective to reflect light in the visible spectrum, said liquid crystal material being capable of being switched between a stable color reflecting state that reflects a maximum reference intensity and a stable light scattering state exhibiting a minimum reference intensity of reflection by application of a voltage pulse, the method comprising the steps of
10 applying voltage pulses of varying magnitude sufficient to achieve a continuum of stable states having color reflectivity of an intensity between said maximum and minimum reference intensities.

10. The improvement according to claim 9 comprising applying square A.C. voltage pulses.

11. The improvement according to claim 9 comprising applying said A.C. pulses at a magnitude between that which will switch said material from said reflecting state to said scattering state.

12. A method of selectively adjusting the intensity of reflection of colored light from a polymer free chiral nematic liquid crystalline light modulating material, including nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount effective to form focal conic and
5 twisted planar textures, said chiral material having a pitch length effective to reflect light in the visible spectrum, said liquid crystal material being capable of

changing textures upon the application of a field, between a maximum and a minimum intensity, the method comprising subjecting said material to an electric field pulse of sufficient duration and voltage to cause a first proportion of said chiral nematic material to exhibit a first optical state and a second proportion of said chiral nematic material to exhibit a second optical state, whereby said material will continuously reflect a selected intensity between said maximum and minimum that is proportional to the amount of said material in said first optical state.

13. The method according to claim 12 wherein said chiral nematic material in said first optical state exhibits a planar texture and said chiral nematic material in said second optical state exhibits a focal conic texture.

14. A light modulating device comprising liquid crystalline light modulating material of chiral nematic liquid crystal consisting essentially of nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount effective to form focal conic and twisted planar textures having a pitch length effective to reflect light in the visible spectrum, wherein said focal conic and twisted planar textures are stabilized in the absence of a field and the liquid crystal material is capable of changing textures upon the application of a field, wherein a first proportion of said material is in a first optical state and second proportion of said material is in a second optical state, and means for establishing an electrical field through said material, said means adapted to provide a pulse of sufficient voltage and duration to change the proportion of said material in said first optical state, whereby the intensity of light reflected may be selectively adjusted.

15. The device according to claim 14 wherein the material in said first optical state exhibits a planar texture and the material in said second optical state exhibits a focal conic texture.

16. The device according to claim 14 including cell wall structure treated to align the liquid crystal.

17. The device according to claim 14, wherein said means for establishing a field through said material is adapted to provide an AC pulse.

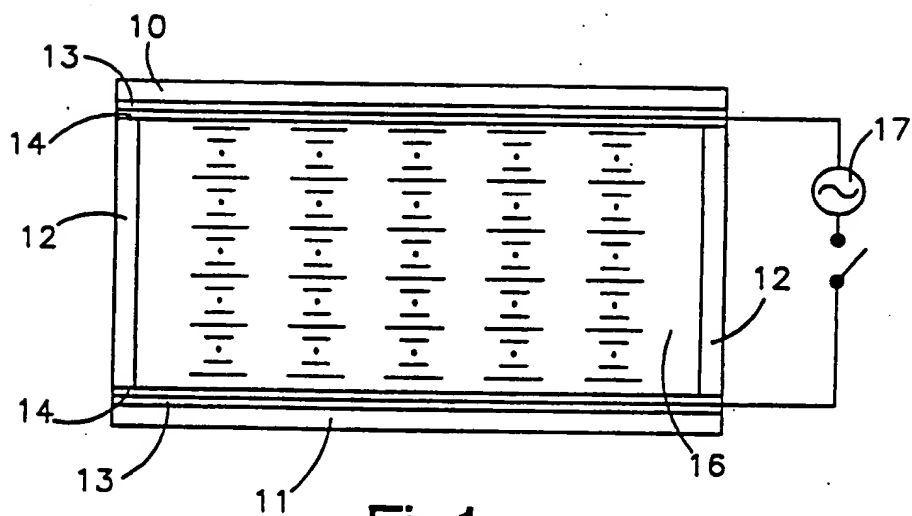


Fig.1

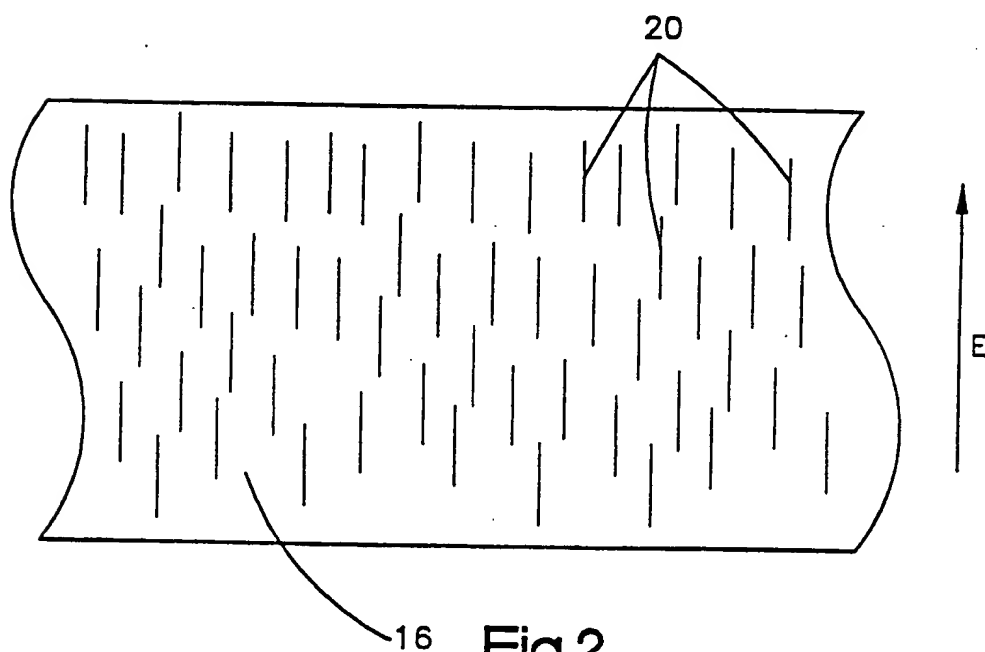


Fig.2

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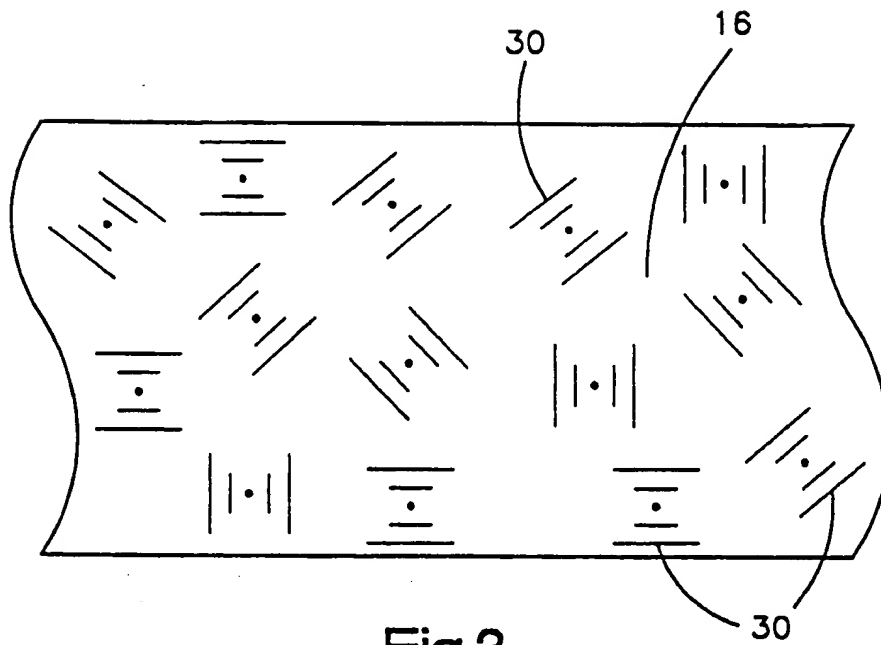


Fig.3

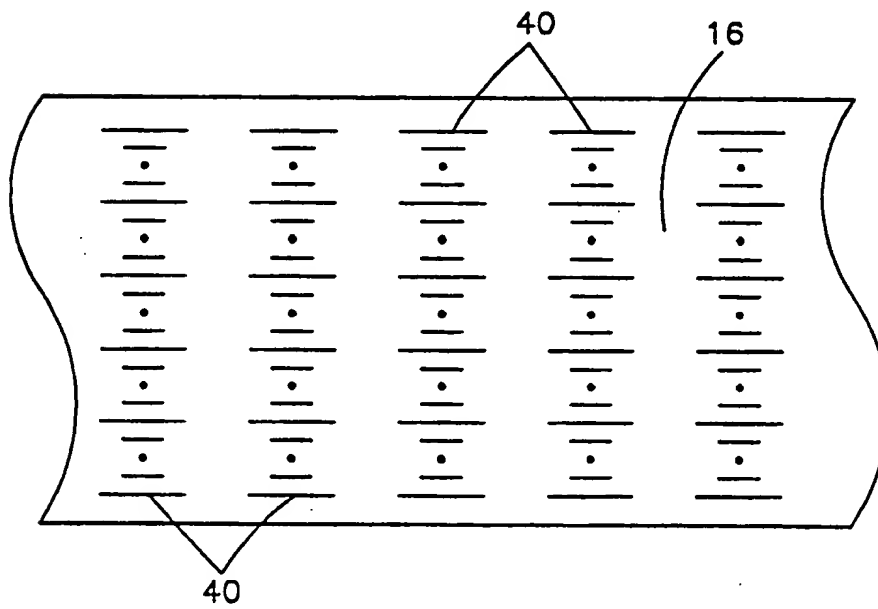


Fig.4

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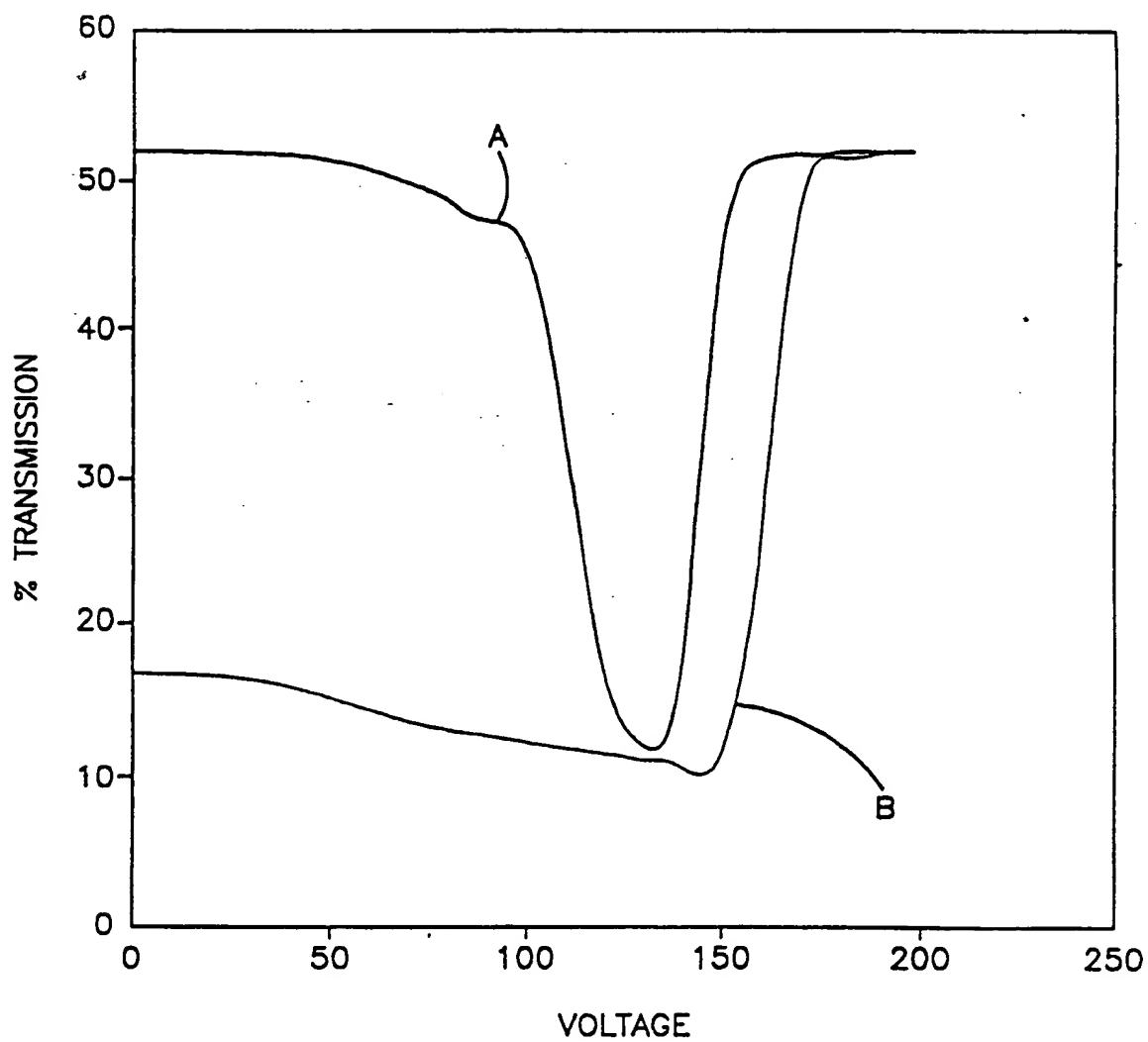


FIG. 5

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INTERNATIONAL SEARCH REPORT

Application No.
PC 93/09999

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : CO9K 19/52; G02F 1/13

US CL : 252/299.01; 359/90, 91, 101

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/299.01; 359/90, 91, 101

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS Text Search - Liquid Crystal with Grey Scale with Chiral Nematic or (Cholesteric).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,097,127 (HAAS ET AL) 27 June 1978, See whole document	1-9, 11-17
Y		10
Y	US,A, 4,408,201 (HARADA) 04 October 1983, See column 1 and column 4, lines 29-37	10
Y	US,A, 3,680,950 (HAAS ETAL.) 01 August 1972, See whole document	1-17
Y	US,A, 3,947,183 (HAAS ET AL.) 30 March 1976, See whole document	1-17
Y	US,A, 3,806,230 (HAAS) 23 April 1974, See whole document	1-17

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T* Inter document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be part of particular relevance	* X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E* earlier document published on or after the international filing date	* Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* &* document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means	
* P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

31 JANUARY 1994

Date of mailing of the international search report

FEB 28 1994

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/09999

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Molecular Crystals and Liquid Crystals, 1973, Greubel et al., Vol. 24, Pages 103-111, "Electric Field Induced Texture changes in Certain Nematic/Cholesteric Liquid Crystal Mixtures" see pages 104-105	9-17